Corrosion

Vol. 11 **September, 1955** **No. 9**

CONTENTS

THIS MONTH'S COVER—This floating marine test rack is located in Corpus Christi Bay. Panels exposed to atmospheric corrosion at 45 degrees face south, while others yield test results in submerged ripple and spray zones. It is operated by Briner Paint Mfg. Co., Inc., Corpus Christi to test new products and for customer service. More information on Page 85 this issue.

☆

Directory of NACE Technical Committees

Technical Practices Committee

C. P. Larrabee, Chairman; Applied Research Laboratory, United States Steel Corporation, Monroeville, Pennsylvania.

E. C. Greco, Vice Chairman; United Gas Corp., Box 1407, Shreveport, La.

W. F. Fair, Jr., Vice President NACE; Koppers Co., Inc., Tar Products Div., Technical Section, 15, Plum St., Verona, Pennsylvania.

Chairmen of T-1 through T-6 also are members of this committee.

T-1   Corrosion in Oil and Gas Well Equipment

W. F. Oxford, Jr., Chairman, Sun Oil Co., Box 2831, Beaumont, Texas.

Jack L. Battle, Vice Chairman, Humble Oil & Refining Co., Box 2180, Houston, Texas

T-1A Corrosion in Oil and Gas Well Equipment, Los Angeles Area

F. W. Schremp, Chairman, California Research Corp., Box 446, La Habra, Calif.

Howard Lorenz, Vice Chairman, Standard Oil Co., 11-C Camp, Taft, Califonia.

T-1B Condensate Well Corrosion

R. C. Buchan, Chairman, Humble Oil & Refining Co., Box 2180, Houston, Texas

W. H. Edwards, Vice Chairman, Superior Oil Company, 400 Oil and Gas Building, Houston, Texas

T-1C Sweet Oil Well Corrosion

H. E. Greenwell, Chairman, Atlantic Refining Co., Box 2819, Dallas Texas

H. E. Waldrip, Vice Chairman, Gulf Oil Corp., 5311 Kirby Dr., Houston, Texas.

T-1D Sour Oil Well Corrosion

J. A. Caldwell, Chairman, Humble Oil & Refining Co., Box 2180, Houston, Texas

R. L. Elkins, Vice Chairman, Shell Oil Corp., Box 1509, Midland, Texas

W. C. Koger, Vice Chairman, Cities Service Oil Company, Cities Service Building, Bartlesville, Okla.

• T-1D-1 Fundamentals of Corrosion

J. D. Sudbury, Chairman, Production Research Division, Development and Research Dept., Continental Oil Company, Ponca City, Oklahoma

T-1F Metallurgy

F. J. Radd, Chairman, Continental Oil Co., Research & Development Lab., Ponca City, Oklahoma

F. L. Current, Vice Chairman, Oil Well Supply Co., Oil City, Pennsylvania

T-1G Sulfide Stress Corrosion Cracking

R. S. Treseder, Chairman, Shell Development Co., 4560 Horton St., Emeryville, California

L. W. Vollmer, Vice Chairman, Gulf Research & Development Corp., Drawer 2038, Pittsburgh, Pa.

T-1H Oil String Casing Corrosion

Jack L. Battle, Chairman, Humble Oil & Refining Co., Box 2180, Houston, Texas.

R. L. Elkins, Vice Chairman, Shell Oil Corp., Box 1509, Midland, Texas.

W. C. Koger, Vice Chairman, Cities Service Oil Company, Cities Service Building, Bartlesville, Okla.

• T-1H-1 Oil String Casing Corrosion, West Texas, New Mexico Area

R. L. Elkins, Chairman, Shell Oil Corp., Box 1509, Midland, Texas.

• T-1H-2 Oil String Casing Corrosion, West Kansas Area

W. C. Koger, Chairman, Cities Service Oil Company, Cities Service Building, Bartlesville Oklahoma.

T-1J Oil Field Structural Plastics

W. M. Thornton, Chairman, Atlantic Refining Co., Box 2819, Dallas, Texas

B. W. Bradley, Vice Chairman, Shell Oil Co., 50 West 50th Street, New York, N. Y.

T-1K Inhibitors For Oil And Gas Wells

J. C. Spalding, Jr., Chairman, Sun Oil Co., Box 2880, Dallas, Texas

E. C. Greco, Vice Chairman, United Gas Corp., Box 1407, Shreveport, Louisiana

T-1M Corrosion of Oil and Gas Well Producing Equipment in Offshore Installations

D. F. Dial, Jr., Chairman, Pure Oil Co., Box 239, Houston, Texas.

F. E. Blount, Vice Chairman, Magnolia Petroleum Co., Box 900, Dallas, Texas

T-2   Pipe Line Corrosion

W. H. Stewart, Chairman, Sun Pipe Line Co., Sun Oil Co., San Jacinto Bldg., Beaumont, Texas.

L. P. Sudrabin, Vice Chairman, Electro Rust-Proofing Corp., Box 178, Newark, New Jersey

T-2A Galvanic Anodes

H. W. Wahlquist, Chairman, Ebasco Services, Inc., 2 Rector Street, New York, N. Y.

T-2B Anodes For Impressed Currents

T. J. Maitland, Chairman, American Tel. & Tel. Co., 32 Sixth Ave., New York 13, New York.

T-2C Minimum Current Requirements

L. P. Sudrabin, Chairman, Electro Rust-Proofing Corp., Box 178, Newark, New Jersey.

R. M. Wainwright, Vice Chairman, University of Illinois, Department of Electrical Engineering, Urbana.

• T-2C-1 Criteria for Cathodic Protection

Francis W. Ringer, Chairman, 7 Hampden Ave., Narberth, Pennsylvania.

T-2D Standardization of Procedures For Measuring Pipe Coating Leakage Conductance

W. E. Huddleston, Chairman, Huddleston Engineering Co., Box 998, Bartlesville, Okla.

L. F. Heverly, Vice Chairman, 2210 W. High St., Lima, Ohio

T-2E Internal Corrosion of Product Pipe Lines and Tanks

Ivy M. Parker, Chairman, Plantation Pipe Line Co., Box 1743, Atlanta, Georgia

A. W. Jasek, Vice Chairman, Humble Pipe Line Co., Drawer 2220, Houston, Texas

T-2F Internal Corrosion of Crude Oil Pipe Lines and Tanks

John C. Watts, Jr., Chairman, Internal Pipe Line Maint. Co., P. O. Box 186, Odessa, Texas

R. L. Elkins, Vice Chairman, Shell Oil Co., Box 1509, Midland, Texas

T-2G Coal Tar Coatings for Underground Use

T. F. P. Kelly, Chairman; Mavor-Kelly Co., 660 M & M Building, Houston 2, Texas

W. F. Fair, Jr., Vice Chairman, Koppers Co., Inc.. Tar Products Div., Tech. Serv., 15 Plum St., Verona, Pa.

T-2H Asphalt Type Pipe Coatings

R. J. Schmidt, Chairman; California Research Corp., 576 Standard Avenue, Richmond, Cal.

P. E. Reynolds, Vice Chairman, Pacific Gas & Electric Co., 245 Market St., San Francisco, California.

T-2J Wrappers for Underground Pipe Line Coating

Clark A. Bailey, Chairman Johns-Manville Sales Corp., 22 East 40th St., New York 16, N. Y.

O. W. Wade, Vice Chairman, Transcontinental Gas Pipe Line Corp., Box 296, Houston, Texas.

T-2K Prefabricated Plastic Film for Pipe Line Coating

F. E. Costanzo, Chairman, 253 Ryan Drive, Pittsburgh 20, Pa.

T-3   GENERAL

F. W. Fink, Chairman, Battelle Memorial Institute, 505 King Ave., Columbus, Ohio.

A. H. Roebuck, Vice-Chairman, Production Research Division, Continental Oil Company, Ponca City, Oklahoma.

T-3A Corrosion Inhibitors

J. L. Wasco, Chairman, The Dow Chemical Co., Bldg. 438, Midland, Michigan

S. K. Coburn, Vice Chairman, Association of American Railroads, 3140 S. Federal St., Chicago, Illinois

T-3B Identification of Corrosion Products

A. H. Roebuck, Chairman, Production Research Division, Continental Oil Company, Ponca City, Okla.

D. A. Vaughan, Vice Chairman, Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio

T-3C Annual Losses Due to Corrosion

F. N. Alquist, Chairman, The Dow Chemical Co., Bldg 438, Midland, Michigan

S. K. Coburn, Vice Chairman, Association of American Railroads, 3140 S. Federal St., Chicago, Ill.

T-3D Instruments For Measuring Corrosion

H. N. Hayward, Chairman, Engineering Experiment Station, University of Illinois, Urbana, Illinois

F. W. Ringer, Vice Chairman, 7 Hampden Ave., Narberth, Pa.

• T-3D-1 Electrical Holiday Inspection of Coatings

Lyle R. Sheppard, Chairman, 6522 Mercer St., Houston, Texas.

T-3E Railroads

R. A. Bardwell, Chairman, Chicago & Eastern Illinois Railroad, Danville, Illinois

G. M. Magee, Vice Chairman, Assoc. Amer. Railroads, Technology Center, Chicago 16, Illinois

• T-3E-1 Corrosion of Railroad Tank Cars

J. R. Spraul, Chairman, General American Transportation Corp., 300 West 151st St., East Chicago, Indiana

C. M. Jekot, Vice Chairman, Lithcote Corporation, 333 West 40th Place, Chicago 9, Ill.

L. R. Honnaker, Vice Chairman, Engineering Materials Group, Engineering Dept., E. I. DuPont de Nemours & Co., Inc., Wilmington, Delaware.

• T-3E-2 Corrosion in Railroad Hopper Cars

Robert Byrne, Chairman, Assoc. Amer. Railroads, 3140 South Federal Street, Chicago 16, Illinois

T-3F Corrosion by High Purity Water

D. J. Depaul, Chairman, Westinghouse Electric Corp., Box 1526, Pittsburgh 30, Pa.

J. F. Eckel, Vice Chairman, General Electric Co., KAPL, Schenectady, New York

T-3G C...
T. P. ..., ternal... 67 W...

T-3H ...
W. S. ..., Chai... 135 E... N. Y.

T-4

F. E. ..., solidat... Inc., ... York

Irwin ... man, ... Powe... Anne...

T-4A ...
Ray M. ..., Univ... partm... neeri...

T-4B C... S...
Irwin ... Dept... Box ... Los ...

D. T. ..., South... Co., ... lanta...

• T-4... Met...
T. J. ..., Ame... Sixth... New ...

• T-4... Pro...
R. M. ..., Ame... Unio... Cleve...

J. P. ..., Cleve... Co., ... 1, Oh...

• T-4...
J. C. H... Serv... 200 ... wood...

D. R. ..., man, ... Co., ... sas C...

• T-4... Typ...
H. W. ..., Islan... Coun... Islan...

J. B. ..., man, ... Co., ...

• T-4... She...
G. H. ..., plex ... Sidne... Mass...

• T-4... Elec...
J. Svet... India... 5265 ... mond...

G. H. ..., man, ... Co., ... diana...

Directory of NACE Technical Committees

T-3G Cathodic Protection

T. P. May, Chairman; The International Nickel Co., Inc., 67 Wall St., New York, N. Y.

T-3H Tanker Corrosion

W. S. Quimby, Temporary Chairman, The Texas Co., 135 East 42nd St., New York, N. Y.

T-4 UTILITIES

F. E. Kulman, Chairman, Consolidated Edison Co. of N. Y., Inc., 4 Irving Place, New York 3, N. Y.

Irwin C. Dietze, Vice Chairman, Dept. of Water & Power, Box 3669, Terminal Annex, Los Angeles, Calif.

T-4A Effects of Electrical Grounding on Corrosion

Ray M. Wainwright, Chairman; University of Illinois, Department of Electrical Engineering, Urbana.

T-4B Corrosion of Cable Sheaths

Irwin C. Dietze, Chairman, Dept. of Water & Power, Box 3669, Terminal Annex, Los Angeles, California

D. T. Rosselle, Vice Chairman, Southern Bell Tel. & Tel. Co., 1432 Hurt Bldg., Atlanta, Ga.

● T-4B-1 Lead and Other Metallic Sheaths

T. J. Maitland, Chairman, American Tel. & Tel. Co., 32 Sixth Ave., New York 13, New York

● T-4B-2 Cathodic Protection

R. M. Lawall, Chairman, Amer. Tel. & Tel. Co., 1538 Union Commerce Bldg., Cleveland 14, Ohio

J. J. Pokorny, Vice Chairman, Cleveland Elec. Illuminating Co., 75 Public Sq., Cleveland 1, Ohio

● T-4B-3 Tests and Surveys

J. C. Howell, Chairman, Public Service Electric & Gas Co., 200 Boyden Ave., Maplewood, New Jersey

D. R. Werner, Vice Chairman, American Tel. & Tel. Co., 324 East 11th St., Kansas City, Missouri.

● T-4B-4 Protection of Pipe Type Cables

H. W. Dieck, Chairman, Long Island Lighting Co., 250 Old Country Road, Mineola, Long Island, N. Y.

J. B. Prime, Jr., Vice-Chairman, Florida Power & Light Co., Box 3100, Miami, Florida

● T-4B-5 Non-Metallic Sheaths and Coatings

G. H. Hunt, Chairman, Simplex Wire & Cable Co., 79 Sidney St., Cambridge 39, Massachusetts

● T-4B-6 Stray Current Electrolysis

J. Svetlik, Chairman, Northern Indiana Public Service Co., 5265 Hohman Ave., Hammond, Indiana

G. H. Cantwell, Vice Chairman, Indiana Bell Telephone Co., 240 N. Meridian St., Indianapolis, Indiana.

T-4D Corrosion By Deicing Salts

M. B. Hart, Chairman, Illinois Bell Telephone Co., 208 West Washington St., Chicago 6, Illinois

J. A. Temmerman, Vice Chairman; City of Rochester, 242 Main Street W., Rochester, New York

T-4E Corrosion by Domestic Waters

T. E. Larson, Chairman, Illinois State Water Survey, Box 232, Urbana, Illinois.

T-4F Materials Selection for Corrosion Mitigation in the Utility Industry

(Chairman resigned. New Chairman to be appointed)

● T-4F-1 Water Meter Corrosion

R. W. Henke, Chairman, Badger Meter Manufacturing Co., 2371 North 30th Street, Milwaukee 45, Wisconsin.

T-5 Corrosion Problems in the Process Industries

Wm. G. Ashbaugh, Chairman, Carbide & Carbon Chemicals Co., Texas City, Texas.

R. I. Zimmerer, Vice-Chairman, Westvaco Chemical Division, Food Machinery & Chemical Corp., Drawer 8127, S. Charleston, West Virginia

T-5A Chemical Manufacturing Industry

R. I. Zimmerer, Chairman, Westvaco Chlor-Alkali Div., Food Machinery & Chemical Corp., Drawer 8127, Charleston 3, West Virginia

A. C. Hamstead, Vice-Chairman, Carbide & Carbon Chemicals Co., South Charleston, West Virginia.

● T-5A-1 Sulfuric Acid

C. L. Bulow, Chairman, Bridgeport Brass Co., 30 Grand St., Bridgeport, Conn.

W. A. Luce, Vice Chairman, The Duriron Co., Box 1019, Dayton, Ohio

● T-5A-3 Acetic Acid

H. O. Teeple, Chairman, The International Nickel Co., Inc., 67 Wall St., New York, New York

● T-5A-4 Chlorine

R. I. Zimmerer, Chairman, Westvaco Chemical Division, Food Machinery & Chemical Corp., Drawer 8127, S. Charleston 3, West Virginia

Wayne Inbody, Vice-Chairman, Diamond Alkali Co., Box 348, Painesville, Ohio

● T-5A-5 Nitric Acid

J. L. English, Chairman, Oak Ridge National Laboratory, Box P, Oak Ridge, Tenn.

W. H. Burton, Vice-Chairman, General Chemical Division, Allied Chemical & Dye Corp., Camden, New Jersey

● T-5A-6 HF Corrosion

T. L. Hoffman, Chairman, Phillips Petroleum Co., Atomic Energy Div., Box 1259, Idaho Falls, Idaho.

T-5B High Temperature Corrosion

John Halbig, Chairman, Armco Steel Corp., Middletown, Ohio.

E. N. Skinner, Vice-Chairman, The International Nickel Co., Inc., 67 Wall St., New York, N. Y.

● T-5B-2 Sulfide Corrosion at High Temperatures and Pressures in the Petroleum Industry

M. E. Holmberg, Chairman, 4101 San Jacinto St., Houston, Texas.

● T-5B-3 Oil Ash Corrosion
(Chairman to be appointed)

● T-5B-4 High Temperature Halogenation

(Chairman to be appointed)

● T-5B-5 Corrosion by Molten Salts and Metals
(Chairman to be appointed)

T-5C Corrosion by Cooling Waters

● T-5C-1 Corrosion by Cooling Waters (South Central Region)

A. S. Krisher, Chairman, Monsanto Chemical Co., Texas City, Texas

C. P. Dillon, Vice-Chairman, Carbide & Carbon Chemicals Co., Texas City, Texas

J. L. Weiss, Secretary, Diamond Alkali Co., Pasadena, Texas

T-5D Plastic Materials of Construction

B. J. Philibert, Chairman, Olin Mathieson Chemical Corp., 820 N. Franklintown Rd., Baltimore, Maryland.

S. W. McIlrath, Vice Chairman, 151 E. 214 St., Euclid 23, Ohio.

● T-5D-1 Questionnaires

B. J. Philibert, Chairman, Mathieson Chemical Corp., Baltimore 3, Maryland

S. W. McIlrath, Vice Chairman, 151 E. 214 Street, Euclid 23, Ohio.

● T-5D-2 Inorganic Acids

Edward Layman, Chairman, Diamond Alkali Company, P. O. Box 686, Pasadena, Texas

R. L. Hughes, Vice Chairman, Spencer Chemical Co., 1231 Woodswether Rd., Kansas City, Missouri

J. F. Malone, Secretary, B. F. Goodrich Chemical Co., 2060 East Ninth Street, Cleveland 15, Ohio

● T-5D-3 Inorganic Alkalies

Peter Kimen, Chairman, Champion Paper & Fibre Co., Box 872, Pasadena, Texas

K. T. Snyder, Vice Chairman, 3730 Griggs Rd., Houston, Texas

L. B. Connelly, Secretary, Eastman Chemical Products Co., 1001 State National Building, Houston 2, Texas

● T-5D-4 Gases

Beaumont Thomas, Chairman, Stebbins Eng. & Mfg. Co., Eastern Blvd., Watertown, New York

J. L. Forse, Vice Chairman, Dow Chemical Company, Plastics Technical Service, Midland, Michigan

William Eakins, Secretary, Chemical Corporation, Platank Division, West Warren, Massachusetts

● T-5D-5 Water and Salt Solutions

J. S. McBride, Chairman, Owens-Corning Fiberglas, 16 E. 56th Street, New York, New York

Paul Elliott, Vice Chairman, Naugatuck Chemical Company, Kralastic Development, Naugatuck, Connecticut

● T-5D-6 Organic Chemicals

R. E. Gackenbach, Chairman, American Cyanamid Company, Calco Chemical Division, Bound Brook, New Jersey

B. E. Pusey, Vice Chairman, Bakelite Co., Div. of U.C.C., Bound Brook, New Jersey

Wade Wolfe, Jr., Secretary, 73 Ermann Drive, Buffalo 17, New York

● T-5D-7 Engineering Design

O. H. Fenner, Chairman, Monsanto Chemical Company, 1700 South Second Street, St. Louis 4, Missouri

K. A. Phillips, Vice Chairman, American Zinc, Lead & Smelting Co., P. O. Box 495, East St. Louis, Illinois

W. B. Meyer, Secretary, St. Louis Metallizing Co., 625 South Sarah, St. Louis 10, Missouri

● T-5D-8 Methods and Criteria for Evaluating Plastics in Chemical Environment

R. F. Clarkson, Chairman, Mathieson Chemical Corp., P. O. Box 552, Pasadena, Texas

R. Lembcke, Secretary, Cities Service Res. & Dev. Co., 920 East Third, Tulsa 3, Oklahoma

T-6 Protective Coatings

A. J. Liebman, Chairman, Pitmar Centrifugal Machine Corp., 1319 Varner Drive, Pittsburgh 27, Pennsylvania

L. L. Whiteneck, Vice Chairman, Long Beach Harbor Dept., 1333 El Embarcadero, Long Beach 2, California.

T-6A Organic Coatings And Linings For Resistance To Chemical Corrosion

R. McFarland, Jr., Chairman, Hills-McCanna Co., 3025 N. W. Ave., Chicago 18, Illinois

C. G. Munger, Vice Chairman, Amercoat Corp., 4809 Firestone Blvd., South Gate, Calif.

L. A. Ferris, Secretary, E. I. DuPont de Nemours & Co., Inc., Polychemicals Dept., Wilmington, Delaware

● T-6A-1 Heavy Linings

H. C. Klein, Chairman, B. F. Goodrich Co., Cuyahoga Falls, Ohio

Positions Available

Wanted: Aggressive corrosion engineer 25 to 35 years, to be division superintendent for cathodic protection engineering and sales company in New Orleans area. Requirements: Experience, travel and desire to make future for self. CORROSION, Box 55-21.

Sales Executive for national corrosion prevention contractor. Knowledge of coatings and cathodic protection with sales background or good contacts essential. Location N. Y. C. Right man eligible for partnership after first year. Replies confidential. CORROSION, Box 55-22.

Engineer—Corrosion: Excellent opportunity with a major oil company located in the Central States for a man who has had prior experience in cathodic protection work on bare and coated pipe lines. CORROSION, Box 55-26.

Directory of Technical Committees

(Continued from Page 5)

- **T-6-2 Vinyl Coatings**
K. Tator, Chairman, 2020 Montour Street, Coraopolis, Pa.

- **T-6A-3 Vinylidene Chloride Polymers**
R. L. Brown, Chairman, The Dow Chemical Co., Midland, Mich.

- **T-6A-4 Phenolics**
F. Baskett, Chairman, 4334 Ella Blvd., Houston, Texas

- **T-6A-5 Polyethylene**
L. S. Van Delinder, Chairman, Carbide & Carbon Chemicals Co., South Charleston, West Va.

- **T-6A-6 Rubber and Elastomers**
H. C. Klein, Chairman, B. F. Goodrich Co., Cuyahoga Falls, Ohio

- **T-6A-7 Silicones**
R. McFarland, Jr., Chairman, Hills-McCanna Co., 3025 N. Western Ave., Chicago, Ill.

- **T-6A-8 Methyacrylates**
L. S. Van Delinder, Chairman, Carbide & Carbon Chemicals Co., South Charleston, West Va.

- **T-6A-9 Furanes**
F. Baskett, Chairman, 4334 Ella Blvd., Houston, Texas

- **T-6A-10 Polyesters**
R. R. Pierce, Chairman, Pennsylvania Salt Mfg. Co., 3 Penn Center Plaza, Philadelphia, Pa.

- **T-6A-11 Epoxys**
C. G. Munger, Chairman, Amercoat Corp., 4809 Firestone Blvd., South Gate, Calif.

- **T-6A-12 Fluorocarbons**
L. A. Ferris, Chairman, E. I. DuPont DeNemours & Co., Inc., Wilmington, Delaware

T-6B Protective Coatings for Resistance to Atmospheric Corrosion

L. L. Sline, Chairman; Sline Industrial Painters, 2612 Gulf Terminal Drive, Houston, Texas.

Howard C. Dick, Vice Chairman, Products Research Service, Inc., Box 6116, New Orleans, Louisiana

T-6C Protective Coatings for Resistance to Marine Corrosion

Raymond P. Devoluy, Chairman, The Glidden Co., Room 1310, 52 Vanderbilt Avenue, New York 17, New York.

R. F. Daw, Vice-Chairman, The Texas Co., 135 East 42nd St., New York 17, N. Y.

T-6E Protective Coatings in Petroleum Production

J. L. Robertson, Chairman, Phillips Petroleum Co., Bartlesville, Oklahoma

T-6G Surface Preparation For Organic Coatings

S. E. Jack, Chairman, Aluminium Laboratories, Ltd., Box 84, Kingston, Ontario, Canada

S. C. Frye, Vice Chairman, Research Dept., Bethlehem Steel Co., Bethlehem, Pa.

T-6H Glass Linings And Vitreous Enamels

G. H. McIntyre, Chairman, Ferro-Enamel Corp., Harvard & 56th Street, Cleveland 5, Ohio

T-6K Corrosion Resistant Construction With Masonry And Allied Materials

L. R. Honnaker, Chairman; E. I. du Pont deNemours & Co., Inc., Engineering Department, Louviers Building, Newark, Del.

George P. Gabriel, Vice-Chairman; Atlas Mineral Products Company, Mertztown, Pa.

T-6R Protective Coatings Research

Robert H. Steiner, Chairman, Naugatuck Chemical Co., Naugatuck, Conn.

Joseph Bigos, Vice-Chairman, Steel Structures Painting Council, Mellon Inst., 4400 Fifth Ave., Pittsburgh 13, Pa.

Positions Available

Graduate Electrical Engineer, experienced in maintenance of electrical controls for pipe line pumping equipment and the design and installation of cathodic protection systems for pipe lines. Travel required. Write P. O. Box 22, Harrisburg, Pa.

Physical chemists, Electrochemists, or Chemical Engineers with training in physical chemistry wanted for research and development. Work will involve laboratory studies of the fundamentals of corrosion chemistry, and analysis of practical corrosion problems that arise in all phases of the petroleum industry. Interest both in fundamentals and in engineering applications necessary. Corrosion experience and knowledge of statistics helpful but not required. Address:

Gulf Research & Development Company
P. O. Drawer 2038
Pittsburgh 30, Pennsylvania

Positions Wanted

Corrosion Engineer—B.S. in Chemistry, age 28, married, 6 years varied chemical and corrosion engineering experience. Now employed in petroleum production corrosion engineering—research, development and application. Seeking greater job responsibilities and future opportunity. CORROSION, Box 55-25.

Positions Wanted

Sales Engineer—Seven years experience technical selling in metropolitan New York area—last three years in protective organic coatings. Corrosion specialist. Chemist, B.S., M.S. Previously instructor of college chemistry. Age 35. Member NACE. CORROSION, Box 55-23.

THE NATIONAL ASSOCIATION OF CORROSION ENGINEERS

is a non-profit, scientific and research association of individuals and companies concerned with corrosion or interested in it, whose objects are:

(a) To promote the prevention of corrosion, thereby curtailing economic waste and conserving natural resources.

(b) To provide forums and media through which experiences with corrosion and its prevention may be reported, discussed and published for the common good.

(c) To encourage special study and research to determine the fundamental causes of corrosion, and to develop new or improved techniques for its prevention.

(d) To correlate study and research on corrosion problems among technical associations to reduce duplication and increase efficiency.

(e) To promote standardization of terminology, techniques, equipment and design in corrosion control.

(f) To contribute to industrial and public safety by promoting the prevention of corrosion as a cause of accidents.

(g) To foster cooperation between individual operators of metallic plant and structures in the joint solution of common corrosion problems.

(h) To invite a wide diversity of membership, thereby insuring reciprocal benefits between industries and governmental groups as well as between individuals and corporations.

It is an incorporated association without capital stock, chartered under the laws of Texas. Its affairs are governed by a Board of Directors, elected by the general membership. Officers and elected directors are nominated by a nominating committee in accordance with the articles of organization. Election is by the membership.

Inquiries regarding membership, and all general correspondence should be directed to the Executive Secretary at the administrative headquarters of the National Association of Corrosion Engineers at 1061 M & M Building, No. 1 Main Street, Houston 2, Texas.

Officers, 1955-56

Topic of the Month

Copper Alloy's Corrosion Resistance to Ammonia Improved by Good Design, Stress Relieving

By I. S. LEVINSON*

COPPER and its alloys always have been considered to be practically useless in ammonic and/or nitrogen bearing solutions. As a matter of fact, ammonia solutions are used in many plants as an alternate for the mercurous nitrate test (ASTM-B-154-51) to discover residual stresses in copper-base wrought products.

Very rarely are the amines, the nitrates, nitrites or other active nitrogen-bearing base chemicals allowed to come in contact with copper materials of construction because of the very rapid attack of the grain boundaries. Intergranular stress corrosion cracking usually is accompanied by some transcrystalline cracking depending on the violence of the failure.

An interesting group of experiments was run on Ampco Grade 8 rolled sheet (ASTM-B-169-Alloy D) to determine behavior under influence of a given concentration of ammonia—and the effects of stress, temperature and time.

A standard solution of 14 percent $NH_4OH(Aq)$ was selected for exposure at atmospheric temperature and at approximately 212 F.

The metal conditions selected were:

1. As received strip.
2. As welded strip.
3. Welded and stress relieved at 850 F.
4. Welded and stress relieved at 1150 F.
5. The above four types, varied by stressing to yield point (or beyond for atmospheric exposures).

Tables 1, 2 and 3 show results obtained.

Several generalizations may be made from this group of tests:

1. More rapid and severe cracking may be expected in the vapor zone than in the liquid zone.
2. Attack due to general chemical combination type of corrosion is more rapid in the liquid zone (supported by weight loss measurements on stress face, heat-treated samples).
3. Increase of temperature increases rate of attack in both vapor and liquid zone.
4. Proper heat treatment definitely improves the resistance to stress corrosion cracking in 14 percent ammonia solution.

* Process Industries, Ampco Metal, Inc., Milwaukee, Wis.

In conclusion it might be said that there is a very interesting observation to be made. Many materials normally considered unsuitable for a given application may become useful with proper design and engineering.

Figure 1—Showing results of immersion tests at room temperature.

TABLE 1—Welded Samples (212 F)

Sample	Zone	Condition	Run 1	Run 2
			RESULTS	
N1	Vapor	As welded	No failure	Crack failure— fusion zone
N3	Vapor	SR @ 850 F	No failure	Small incipient cracks
N5	Vapor	SR @ 1150 F	No failure	No failure
N2	Liquid	As welded	No failure	Incipient cracks
N4	Liquid	SR @ 850 F	No failure	No failure
N6	Liquid	SR @ 1150 F	No failure	No failure

Note: Run 1 was 80 hours. Run 2 was 120 additional hours with fresh solution.

TABLE 2—Sheet Samples

Sample	Zone	Condition	Run 1	Run 2
			RESULTS	
N7	Vapor	As stressed	No failure	Crack failure
N9	Vapor	SR @ 850 F	No failure	No failure
N11	Vapor	SR @ 1150 F	No failure	No failure
N8	Liquid	As stressed	No failure	No failure
N10	Liquid	SR @ 850 F	No failure	No failure
N12	Liquid	SR @ 1150 F	No failure	No failure

Note: SR indicates stress relief. Samples were stressed and then heat treated.

TABLE 3—Total Immersion at Room Temperature

Sample	Condition	Exposure Time	Result
1	As stressed	5 days	Cracked at center
2	1150 F SR	12 days	No failure

365t

Principles Applicable to the Oxidation And Corrosion of Metals and Alloys*

By W. W. SMELTZER

Introduction

SINCE the studies on the surface oxidation of metals by Tammann[1] and Pilling and Bedworth[2] in the early 1920s, extensive research has been completed to elucidate the manner and rates of growth, structure and various physiochemical properties of oxide films on metals. Applied and basic research is in active progress in this field and, although much further knowledge is required, many principles of value in the study of corrosion have been established. Because of the increasing application of metals in high temperature environments considerable research effort is being expended on the development of suitable alloys resistant to oxidation. In fretting corrosion, emphasis is being placed on studies to elucidate the role of the oxide film. Recently, in electrochemical corrosion, concepts applicable to the formation of oxide films have been introduced to explain the initiation of corrosion in mildly corrosive environments. Principles applicable to formation of oxide films and their role in wet corrosion of metals are outlined in this review.

Film Structure and Oxidation Rate Laws

1. General

The resistance of a metal to oxidation depends upon the nature of the film formed on the surface. Oxidation rates may follow specific types of curves; the equations of these curves are designated "oxidation rate laws." These rate laws are shown in Table 1 and represented graphically in Figure 1.

The linear and inverse logarithmic relationships represent the extreme cases of surface oxide formation as the former rate is constant regardless of thickness whereas the latter rate slows to a negligible value.

At low temperatures many metals form a thin (10 to 50Å) stable film according to an inverse logarithmic law. At intermediate temperatures (100-300 C) film growth on metals may continue by any of the above laws and at sufficiently high temperatures oxide growth generally occurs by a parabolic or linear rate.

These oxidation rate laws can be derived from assumptions about the structure of the oxide film. Two types of models are commonly used. The first assumes the formation of a continuous compact film in which the reaction rate is controlled by diffusion of ions and electrons through lattice defects in the film. These lattice defects consist of metallic ions in interstitial lattice positions, cation vacancies and electron holes. The second assumes the formation of

W. W. SMELTZER—He holds a BSc degree in chemistry from Queen's University, Kingston, Canada and a PhD degree in physical chemistry from the University of Toronto. His graduate research consisted of physical adsorption studies. He has worked in the fields of heterogeneous catalysis and chemisorption at the National Research Council Laboratories, Ottawa. Since 1953 he has been a member of the staff of the Chemical Division, Aluminium Laboratories, Ltd., Kingston where he is working in the field of formation of oxide films on aluminum and its alloys.

Abstract

Phenomenological basis of kinetic laws governing oxidation is described to illustrate manner of growth and protective properties of oxide films on metals. Metals are separated into groups forming "metal-excess" and "metal-deficit" oxide films and emphasis is placed on role of lattice defects in governing diffusion of metal through film to react with environment. Effects of alloying elements on oxidation rates of metals are discussed in terms of formation of films consisting of heterogeneous mixtures and solid solutions of oxides and intramolecular oxides. Special reference is made to aluminum and its alloys for illustrative examples. 13 figures, 59 references.
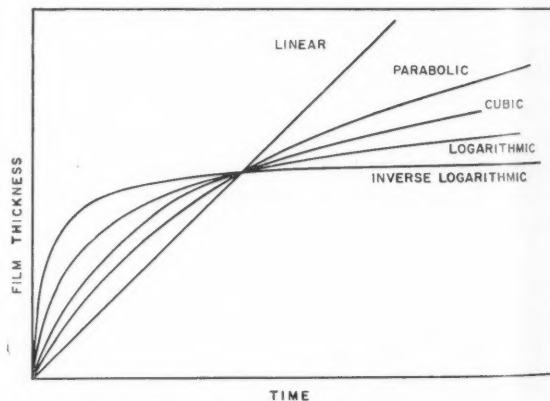
Figure 1—Oxidation rate laws.

TABLE 1—Oxidation Rate Laws

Oxidation Rate Law	Differential Equation	Integral Form	
Parabolic	$dx/dt = k_1/x$	$x^2 = K_1t + K_2$	(1)
Cubic	$dx/dt = k_2/x^2$	$x^3 = K_3t + K_4$	(2)
Logarithmic	$dx/dt = k_3 \exp. - k_4x$	$x = K_5 \log (K_6t + k_7)$	(3)
Inverse Logarithmic	$dx/dt = k_5 \sinh k_6/x$	$1/x = K_8 - K_9 \log t$	(4)
Linear	$dx/dt = k_7$	$x = K_{10}t + K_{11}$	(5)

x is film thickness, t is time, and $k_1 — k_7$, $K_1 — K_{11}$ are constants.

a less perfect film with macroscopic defects such as blisters, cracks and pores which give preferential oxidation paths. In this model, depending on film

---

OXYGEN

OXIDE

METAL   M$^+$ – INTERSTITIAL
e$^-$ – ELECTRON
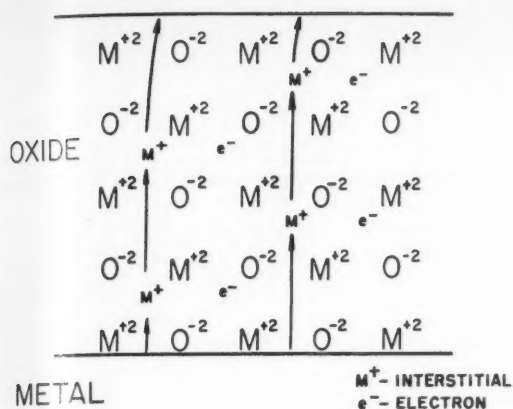
Figure 2—Cubic divalent metal-excess oxide film.

OXYGEN

OXIDE

METAL   □ – CATION VACANCY
M^{+3} – ELECTRON HOLE

Figure 3—Cubic divalent metal-deficit oxide film.

structure, lattice defects may also play an important role.

2. Model of Compact Oxide Film with Lattice Defects

a) Classification of Metallic Oxides

The type of lattice defect structure of a metal oxide must be identified in order to interpret the mechanism of film growth. Surface oxide films are classified according to the properties of their bulk crystalline oxides because, at ordinary temperatures, metallic oxides are not of exact stoichiometric composition. A "metal-excess" oxide is defined as containing an excess of metal atoms in the form of cations in interstitial lattice positions and a corresponding excess of free electrons. This is illustrated for a cubic divalent metal oxide in Figure 2. Film growth occurs by diffusion of metallic ions through the interstitial lattice positions from the metal to the gas/oxide interface and of free electrons to react with oxygen. Conversely, a "metal-deficit" oxide is defined as being deficient in metallic ions and so contains vacant lattice sites. This is illustrated for a cubic divalent metal oxide in Figure 3. To maintain electrical neutrality, there is an equal deficiency of electrons from lattice positions which are designated as "electron holes." The removal of an electron from a metal ion places it in a higher valence state and thus "electron holes" consist of such ions. In this case, metallic ions diffuse from the metal through the cation vacancies in the film to the oxide/oxygen interface to combine with oxygen. ZnO, CdO, Al$_2$O$_3$ are metal-excess oxides whereas Bi$_2$O$_3$, Cr$_2$O$_3$, CoO, FeO, Cu$_2$O and NiO are metal-deficit oxides. This classification of metallic oxides is of decisive importance for interpreting oxidation reactions because the reaction rate is dependent on the concentrations and mobilities of ions in defect positions.

b) Wagner, and Gulbransen and Andrew Theories of Parabolic Oxidation

It was known from the work of Tammann and of Pilling and Bedworth that a parabolic law governed the formation of a compact oxide layer. In 1933
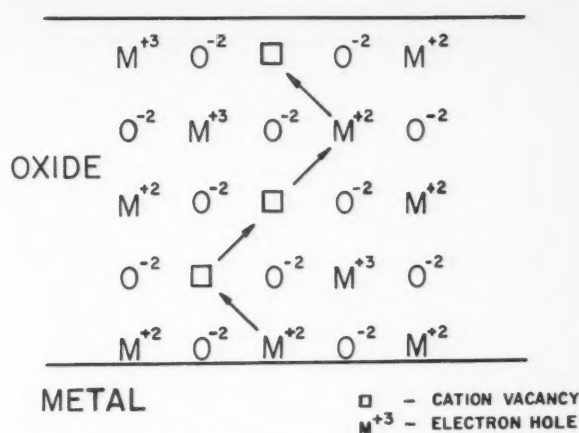
Wagner[3] applied the model first described and assumed that the rate determining step in the oxidation was the diffusion of metal ions through lattice defects in a compact film. Wagner[4] has presented a review of this theory by which the parabolic rate constant is expressed in terms of electrical transport quantities.

The equation for the parabolic law may be derived simply as follows. Assuming that there is no electrical field across the oxide layer (this can be done in the case of thick films) the ion current is,

$$j = -D \frac{dn}{dx} \qquad (6$$

where D is the diffusion coefficient and dn/dx is the concentration gradient of interstitial ions or cation vacancies. Thus, the rate of film growth is,

$$\frac{dx}{dt} = j\Omega = -D\Omega dn/dx \qquad (7$$

if Ω is the volume of oxide per metal ion. Since the concentration gradient is inversely proportional to the film thickness, integration gives the equation of the parabolic law

Here, $X^2 = K_1 t + K_2$
$K_1 = 2\Omega D (n_1 - n_2)$ and $K_2 = 0$ (1

if n_1 and n_2 are the number of interstitial ions or vacancies per cubic centimeter at the oxide/oxygen and oxide/metal interfaces.

This theory has been developed further by Gulbransen and Andrew,[5] and Gulbransen[6] who assumed that the concentrations of interstitial ions in metal-excess oxides or vacancies in metal deficit oxides may be expressed in terms of the standard free energy change for the dissociation reaction of the metallic oxide and that the value of the diffusion coefficient may be calculated from classical diffusion theory. The magnitude of the parabolic rate constant, K_1, can be calculated if the free energies for formation and diffusion of the defects can be expressed in terms of their heats and entropies. The calculated values of the parabolic constants for a

given metal may be compared to the experimentally determined value to verify the validity of the assumed model.

The preceding methods have not been applied extensively to many metals due to lack of sufficient thermodynamic data and values of physical parameters for their oxides. In these cases, the following equation derived from transition state theory by Gulbransen[7] is used to express the parabolic constant:

$$K_1 = \frac{2kT}{h} \lambda^2 \exp. \triangle S^*/R - \triangle H^*/RT \qquad (9$$

where $\triangle H^*$ and $\triangle S^*$ are the activation energy and entropy of reaction respectively, k is Boltzmann's constant, R is the gas constant, h is Plank's constant and λ is the interatomic distance between diffusion sites. This expression is useful because the values of the activation energy and entropy of reaction can be used to classify oxidation characteristics of different metals.[8, 9]

c) Mott and Cabrera Theory of Metal Oxidation

The parabolic law of oxidation can also be derived from the concepts of Mott,[10] and Cabrera and Mott[11] which can be employed also to derive the inverse logarithmic and cubic laws. This theory is based on the first model—that of a compact film with lattice defects. Consideration must be given to the electrical field, which due to the contact potential between the metal and the oxide film, influences the manner of film growth to a degree dependent upon its thickness. Concepts are presented which are applicable to the formation of a "metal-excess" oxide film.

The potential energy diagrams of metal ions and electrons in a metal-excess oxide film with a surface layer of adsorbed oxygen are illustrated in Figures 4 and 5 respectively. Figure 4a shows the energy levels before electrons have passed through the film. There are vacant electron levels in the adsorbed oxygen atoms below (by energy eV) the Fermi level of electrons in the metal. Accordingly electrons flow from the metal (over or through the potential energy barrier ϕ by thermionic emission or tunnel effect) to the empty oxygen levels until the steady state represented by Figure 4b is reached. An electrical field (eV/x) now exists across the oxide film which aids the diffusion of the metal ions. For film growth, metal ions must escape over the potential barrier, W, of Figure 5 and diffuse through interstitial positions in the oxide to react with adsorbed oxygen. The rate of escape of metal ions with these conditions is proportional to the Boltzmann factor,

$$\exp. - W/kT \exp. q_1 a_1 F/kT \qquad (10$$

where F is the electrical field, q_i is the electrical charge of a metal cation and a_i is the half width of the potential barrier.

This field is so strong across very thin films (less than 100 Å) that no approximation can be made for the Boltzmann factor. Thus, the rate of film growth is,

$$\frac{dx}{dt} = j\Omega = N^* \Omega v \exp. - W/kT \exp. q_1 a_1 F/kT \qquad (11$$

where N^* is the number of metal atoms per square centimeter suitably located for movement from the metal into the oxide film and v is the frequency of
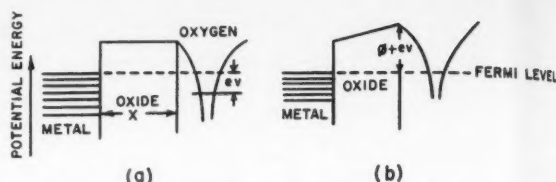
Figure 4—Electronic levels in metal, oxide and adsorbed oxygen[11] (a) Before electrons have passed through oxide. (b) When equilibrium is set up.
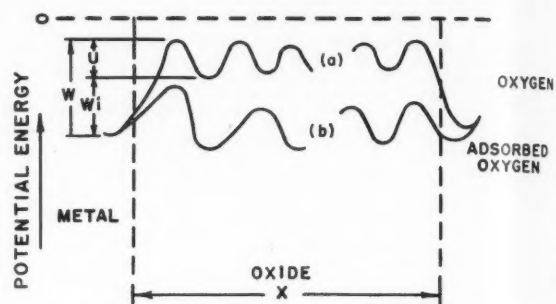
Figure 5—Energies of ions for metal-excess oxide[11] (a) Ions in interstitial positions. (b) Ions in normal positions.

vibration of the metal lattice. This expression leads to the inverse logarithmic law of oxidation, equation (3 and Figure 1.

At intermediate film thicknesses the condition may arise that $q_i a_i F << kT$ and the diffusion velocity of ions is then proportional to the electrical field. i.e. an approximation can now be made for the Boltzmann factor. Hence, the rate of film growth is,

$$\frac{dx}{dt} = j\Omega = \Omega n_i v_i \, V/x \qquad (12$$

where v_i is the mobility of the interstitial ions. In this instance, the parabolic rate constant is,

$$K_1 = \frac{V\Omega q_i v}{a_i kT} \exp. - W/kT \qquad (13$$

The effect of the electrical field is negligible for thick films and the parabolic rate constant of equation 8 governs film growth. According to this theory. the equation for the parabolic rate constant is,

$$K_1 = 2\Omega(N_i N_e)^{1/2} a_i^2 v \exp. - \frac{1}{2} (W_i + \phi) - U/kT \qquad (14$$

Here, N_i and N_e are the concentrations of interstitial positions in the oxide and electrons in the metal. respectively.

It is to be noted that the expressions for the parabolic rate constant of equations 9, 13 and 14 are of Arrhenius form

$$K_1 = A \exp. - E/RT \qquad (15$$

where A is the frequency factor and E the activation energy of reaction. Thus, this energy term can be determined from the temperature coefficient of the parabolic rate constants.

3) Model of Oxide Film with Macroscopic Defects

The second type of model is assumed to be a film containing macroscopic defects as well as the lattice defects already discussed. Macroscopic defects are assumed to be pores, cracks and blisters and are believed to be caused by internal film stresses, the existence of which has been proved.[12, 13] Several
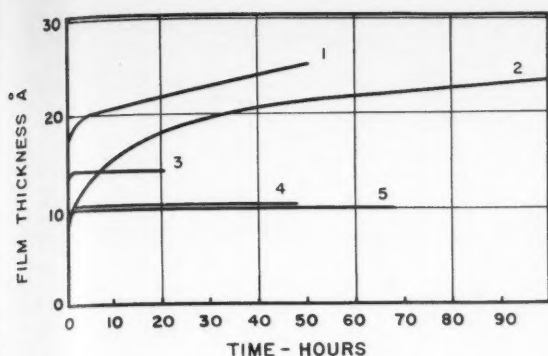
Figure 6—Oxide formation on evaporated aluminum films in dry oxygen at room temperature. References: Curve 1[11]; curve 2[22]; curve 3, 5[26]; curve 4[27].
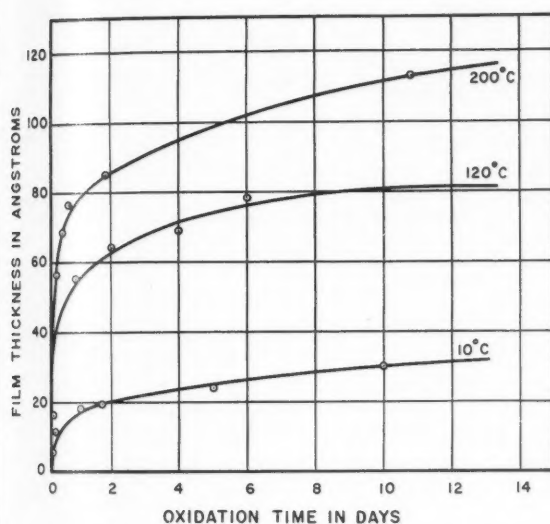
Figure 7—Oxide formation on evaporated aluminum films in dry oxygen in temperature range 10-200 C[22].

models of oxide films containing macroscopic defects have been advanced to explain the occurrence of linear and logarithmic rate laws.

With an imperfect film, macro-defects may offer no resistance to the passage of gas molecules to the metal surface. Thus, oxidation will proceed by a linear law if the reaction rate remains constant. This view has resulted in the Pilling and Bedworth rule[2] of metal oxidation that a metal may obey a linear law if its oxide occupies a smaller volume than that of the consumed metal. It has been suggested also that a metal which forms an oxide of larger volume than that of consumed metal may obey a linear law if stress relief causes breakdown of the film. This breakdown may be complete[12, 14] or partial resulting in the formation of porous oxide over a compact film of constant thickness.[15] In the latter case, the rate controlling factor is the diffusion of ions though the lattice defects in the compact film and the rate is again constant. At present, these explanations of the linear law of oxidation have not been confirmed experimentally.[16]

A different condition is assumed to develop when

oxidation of the metal at the base of a macroscopic defect blocks it and produces a certain small chance of film rearrangement and blocking at other defects in its neighborhood.[17] In this instance, the number of macro-defects decreases as oxidation proceeds and is proportional to the quantity of oxygen consumed. This leads to a decreasing rate of oxidation with time and mathematical derivation from these assumptions yields the logarithmic law of oxidation equation (3 and Figure 1. This law of oxidation also may be derived for a film containing a random network of blisters.[14]

Oxidation of Aluminum

1. *General*

The oxidation of aluminum may be selected as one specific case to illustrate the applicability and limitations of metal oxidation principles. Although further information is required, considerable knowledge of its oxide film properties have been obtained by analyzing oxidation results according to the principles formulated to explain oxidation rate laws. Aluminum is assumed to form a compact "metal-excess" oxide film because its oxidation rate is largely independent of oxygen pressure[18] and ultraviolet radiation.[19] If this model provides an adequate description of the actual oxide film, oxidation proceeds by diffusion of metal ions through interstitial lattice positions and electrons to the oxide/gas interface where reaction occurs. Consequently, the Mott and Cabrera theory has been applied extensively to the oxidation of aluminum.[11, 19-25]

2. *Film Growth*

Aluminum forms a thin, compact film on its surface upon exposure to oxygen. Its formation on evaporated aluminum films at room temperatures is shown in Figure 6. Oxidation occurs rapidly for about one hour and then decreases to a very low value and, although there are large variations in the determinations, the final oxide film thickness is less than 30 Å. In fact, the two curves for growth of 10 Å oxide films indicate that the thickness may approach the dimensions of a unimolecular layer of alumina. The curves of Figure 7 show that the rate of film growth remains small up to temperatures of 200 C and the limiting film thickness is a few hundred angstroms. Above 400 C, Figure 8, the initial rapid rate of oxidation is followed by an approximately constant rate for a period which is dependent upon the temperature. This latter rate, even at the elevated temperature of 600 C, then slows to a low value at a film thickness of approximately 2000 Å.[2, 28]

The virtual cessation of further oxidation at higher temperatures when a limiting film thickness has been reached is probably due to change in film structure. The aluminum oxide film is amorphous at temperatures below 400 C; above this temperature, gamma-alumina with a spinel crystalline structure predominates.[18, 29-34] As ionic diffusion through such structures is known to be slow, the formation of gamma-alumina would be expected to decrease the rate of oxidation.

Evidence in support of film crystallization decreasing the rate of oxidation is presented in the curves

of Figure 9. These show oxidation rates at 500 C for metallographically polished aluminum after vacuum annealing at various temperatures and for varying times. It is evident that raising the annealing temperatures or increasing greatly the duration of heating at a given temperature decreases the subsequent rate of oxidation—presumably as a result of film crystallization during annealing.

3. Oxidation Mechanism

Aluminum is assumed to form a compact metal-excess oxide film. Values have been determined experimentally for the height and width of the ion and electron diffusion barriers and the energy and entropy of activation. Some of the values have been calculated from gaseous oxidation rate data while others have been obtained from anodic oxidation studies in an ammonium borate solution.[24, 25] The latter is possible since in this electrolyte a compact anodic film is formed, the rate depending on the diffusion of metal ions and electrons and the same laws governing film growth apply as for gaseous oxidation. Values for these energetic factors, taken from the literature and from work at Aluminium Laboratories Limited, Kingston, are recorded in Table 2.

Since the energy barrier against metal ion diffusion is higher than the barrier against electron diffusion, (1.6-1.8 vs 0.6 e.v.) it follows that the rate controlling factor is the diffusion rate of metal ions through the film. This being so, the energy value for the metal ion diffusion barrier can be used to predict the effect of temperature on oxide film growth. Mott and Cabrera assumed an inverse logarithmic rate law for the oxidation of aluminum at low temperatures. The curves in Figure 6 show that this is reasonable. Thus equation (11 applies

$$\frac{dx}{dt} = N^* \, \Omega v \, \exp. - W/kT \, \exp. \, q_1 a_1 F/kT \qquad (11$$

As the thickness approaches about 20 Å the rate of oxidation virtually ceases. If this rate of formation is taken to be one atomic layer of oxide per day (about 10^{-13} cm./sec.) at this thickness, N^* is assumed to be 10^{15}/cm.², v to be 10^{12}/sec. and Ω to be 3×10^{-23} cm.³ equation (11 reduces to:

$$X_L = Va_1q_1/W - 39 \, kT \qquad (16$$

where X_L is the limiting film thickness. This relates the limiting film thickness to the temperature.

Equation (16 indicates that if the thermal energy, 39 kT, approaches the value of W, the ion diffusion barrier, X_L does not approach a finite limit. If W = 1.8 e.v. the temperature at which this occurs is about 300 C. Confirmation of this is obtained from anodic
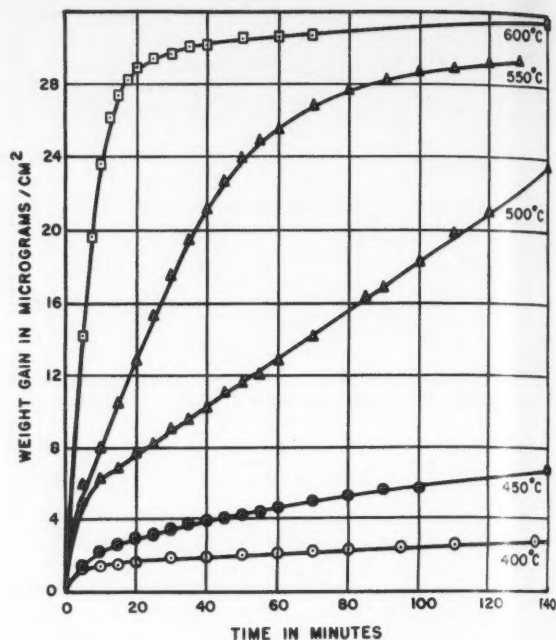
Figure 8—Oxide formation on metallographically polished aluminum in dry oxygen in temperature range 400-600 C.
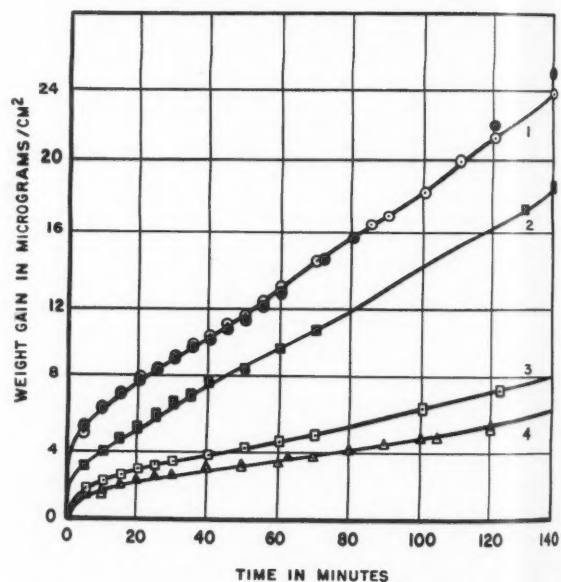
Figure 9—Oxide formation on metallographically polished aluminum specimens in dry oxygen at 500 C. Curve 1—Vacuum annealed 30 minutes at 500 C; curve 2—Vacuum annealed 60 minutes at 500 C; curve 3—Vacuum annealed 30 minutes at 600 C; curve 4—Vacuum annealed 1 and 2 hours at 600 C.

TABLE 2—Energy Terms Governing Oxidation Rate of Aluminum

Oxidation Method	Reference	Ion Diffusion Barrier W-e.v.	Electron Diffusion Barrier φ-e.v.	Width of Potential Barrier a-Å	Energy of Activation E-Kcal/mole		Entropy of Activation △ S-cal/mole	
					Thin Film	Thick Film	Thin Film	Thick Film
Anodic.....	(24)	1.55,—1.8		2.5,—3.5				
Anodic.....	(25)		0.6	1.5				
Oxygen.....	Metallographically Polished Samples Annealed at 500 C				37.9	41.0	—7.3	—2.5
	Metallographically Polished Samples Annealed at 600 C				41.0	50.7	—4.0	8.9
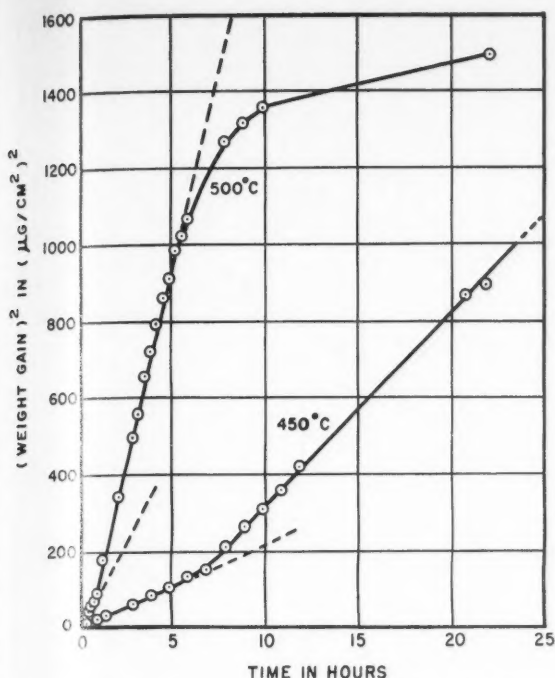
Figure 10—Parabolic plots of oxidation data at 450 C and 500 C for metallographically polished aluminum.

oxidation film studies which also predict a non-limiting rate of formation above 300 C.[24]

The Mott and Cabrera theory predicts that the growth of the compact film should continue according to a parabolic law of oxidation at elevated temperatures. If the data are plotted on a parabolic scale, $(gm./cm.^2)^2$ as a function of time, two linear sections in the curve may be obtained because the rate constants may vary for thin and thick films. To check the validity of this oxidation rate data obtained at 450 C and 500 C have been plotted on a parabolic scale in Figure 10. The curves do show two linear regions with that for the thicker film having the higher rate constant. According to the Mott and Cabrera theory this is because the energy of activation for thick films is less than for thin films. The energy of activation can be calculated from the temperature coefficient of the rate constants. This was done for the curves at 450 and 500 C and for other curves in the temperature range 400-600 C and the activation energies shown in Table 2 were calculated.

The height of the potential barrier against ion diffusion, W, corresponds to the energy of activation for parabolic oxidation in the thin film region (equation (13). The height of this barrier of 1.6-1.8 e.v., determined from anodic oxidation data, is equal to an activation energy of 36.7-42.5 Kcal./mole. This agrees well with the value 37.9-41.0 Kcal./mole calculated from gaseous oxidation data in the thin film region and lends weight to the model of the oxide film in which oxidation is controlled by diffusion of metallic ions over the potential barrier at the metal/oxide interface.

The higher values of 41.0-50.7 Kcal./mole for the activation energy as the film thickens do not sub-

stantiate the suggestion that this term should be less for thick films (equation (13 and (14). Also, the entropy of activation values calculated from equation (9 increase as the film thickens. It is suggested that these two findings may be explained by modifying the oxide film model somewhat.

The aluminum oxide film is amorphous at temperatures below 400 C and tends to crystallize above this temperature. If the amorphous film consists of Al_4O_6 molecular groups,[33] crystallization will probably produce gamma-alumina as the predominating crystalline phase. Metal ions may diffuse by two paths in the amorphous film—either through interstitial positions in the molecular groups or along the group boundaries. As crystallization proceeds the number of boundaries is decreased and hence the ionic diffusion along these paths is reduced. This has the effect of increasing the potential barrier against ion diffusion if the potential energy barrier against ion diffusion is less for these paths than through interstitial lattice positions of the crystalline oxide. Large negative values of the reaction entropy of activation have been explained by assuming the presence of short-circuiting diffusion paths in the oxide film.[6] If, as suggested, crystallization reduces the boundary paths this may account for the increase noted for the entropy term. Although this type of analysis is open to question, support for these views on the effect of crystallization is found in a reduction of oxidation rates of aluminum vacuum annealed for relatively longer times and higher temperatures (Figure 9).

Oxidation of Alloys

1. *General*

The ratio of metallic elements in the surface oxide on an alloy is usually different from that in the bulk alloy; consequently oxidation rates and surface properties are dependent on the composition and structure of the surface oxide rather than of the underlying metal. The surface oxide layer may consist of heterogeneous mixtures, solid solutions and intramolecular oxides. Study of such surface layers has led to principles for the prevention of oxidation and corrosion which serve as valuable guides for selection of alloying metals. In the following, aluminum alloys and metals with aluminum as an alloying constituent are used for illustrative examples.

2. *Heterogeneous Mixtures of Oxides*

The oxidation rate of a metal frequently can be decreased by the addition of an alloying element which reacts preferentially with oxygen to form an oxide layer through which the diffusion rate of the reactants is less than in the oxide of the pure metal. Suitable alloying metals form oxides possessing a low electrical conductivity and a volume ratio of oxide to metal greater than unity. This is due to the fact that the electrical conductivity of metal oxides is determined by the concentrations of ions in defect positions and electrons, which are, in turn, instrumental in determining the growth character for compact oxide layers.

Two distinct types of surface oxide scales may result from this type of oxidation. The first type con-

sists of a layer of oxide of the alloying element on the metal surface and requires that the oxidation be carried out at high temperatures or in a specific oxidizing environment. The use of an environment in which the partial pressure of oxygen is less than the dissociation pressure of the oxide of the pure metal has been used for this purpose and is termed "selective oxidation."[35] For example, a protective aluminum oxide layer has been formed on copper and silver containing aluminum by heating these alloys in a hydrogen atmosphere containing water vapor.[35, 36]

The second and more general type of oxide scale consists of an outermost oxide layer of the pure metal and an inner layer of oxide particles of the alloying constituent, dispersed in the metal. This type of scale formation is designated internal oxidation and has been the topic of a series of reviews.[37-39] Iron, copper and nickel alloyed with aluminum tend to form an internal subscale of alumina.

Heterogeneous oxide films are not always more protective against oxidation. A case in point is the aluminum-magnesium alloy system for which oxidation proceeds at an appreciable rate for longer times than for aluminum.[40-47] This is illustrated by the curves of Figure 11 which show first, the oxidation at 550 C of super purity aluminum and second, that of its alloy containing 2.87 percent magnesium. This second curve exhibits an initial curvilinear portion followed by a linear remainder and is similar to oxidation rate curves obtained for magnesium and magnesium alloys containing aluminum.[43] The linear oxidation rate of magnesium and magnesium rich alloys is believed to be due to the formation of a porous oxide layer which allows oxygen molecules to penetrate to the metal surface. With magnesium oxide the oxide/metal molar volume ratio is less than unity and this tends to make the layer non-protective. It is possible that the behavior of the aluminum-3% magnesium alloy is due to the formation of a porous oxide layer of magnesia over an Al_2O_3 or Al_2O_3-MgO compact film next to the metal. Support for this view is obtained from diffraction studies.[32]

A trace of beryllium added to aluminum-magnesium alloys effects a marked reduction in their oxidation rates.[42, 48] Beryllium oxide has a very low electrical conductivity and an oxide-to-metal ratio greater than unity. It is believed that it oxidizes preferentially and forms a compact protective film of either pure oxide or an intramolecular oxide. Also, the oxidation of these alloys during heat-treatment may be reduced by small quantities of hydrofluoric acid or by volatilizing sodium fluoborate into the furnace atmosphere.[44, 47]

3. *Oxide Solid Solutions*

The oxidation rate of a metal may also, in certain cases, be decreased by the addition of an alloying element if its oxide is soluble in the oxide of the metal.[49-52] For a metal covered with a "metal-excess" oxide, an alloying element is effective if its oxide dissolves in the metal oxide to give higher valency ions than the solvent metal. For example, the addition of aluminum (+3) decreases the oxidation rate of zinc
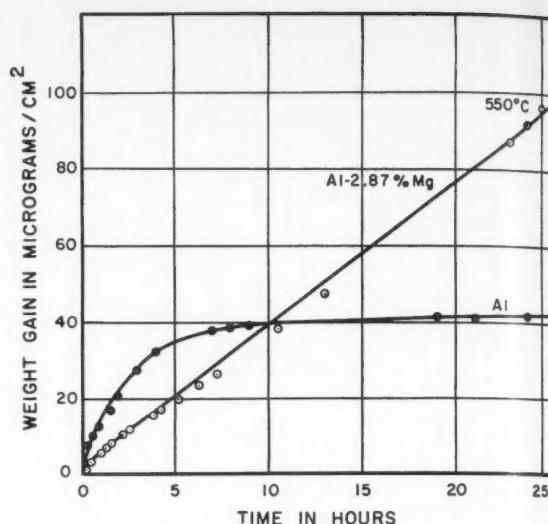
Figure 11—Oxide formation on metallographically polished aluminum and aluminum-2.87 percent magnesium at 550 C.

TABLE 3
Parabolic Rate Constants for Oxidation of Zinc-Aluminum Alloys[49]

Zinc Alloys in Atom Percent	Rate Constant of Oxidation K gm² cm⁻⁴ hr⁻¹	
	Observed	Calculated
Zinc	0.8×10^{-9}	
Zinc—0.1 Al	1.0×10^{-11}	4×10^{-11}
Zinc—1.0 Al	$<1.0 \times 10^{-11}$	4×10^{-12}

(+2). On the other hand, the rate of oxidation of a metal covered with a "metal-deficit" oxide can be decreased by addition of an alloying metal which forms lower valency cations than the solvent metal.

For example, the addition of lithium (+1) decreases the oxidation rate of nickel (+3).

The alterations in oxidation rates by solid solution formation of oxides are interpreted on the basis of the model of a compact oxide layer with lattice defects. If a zinc-aluminum alloy is oxidized at 400 C, a layer of zinc oxide containing aluminum oxide in solid solution is formed. The aluminum ions take up lattice positions in the film as shown in Figure 12 and decrease the concentration of interstitial zinc ions according to the following equation,

$$\tfrac{1}{2}O_2 + 2Zn^+_{(1)} + Al_2O_3 \rightarrow 2\,Al^{+++}_{Zn(1)} + 4\,ZnO \quad (17$$
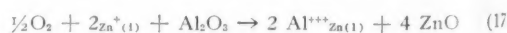
This decrease in the concentration of interstitial zinc ions causes a corresponding decrease in the oxidation rate. Oxidation of these alloys follows a parabolic law at 400 C, the rate constant for which can be calculated from electrical conductivity and thermodynamic data with the assumption of the above relation. As shown in Table 3, the calculated values are in excellent agreement with those determined experimentally and this lends weight to use of the postulated film model.

This concept of the influence of mutual solubility
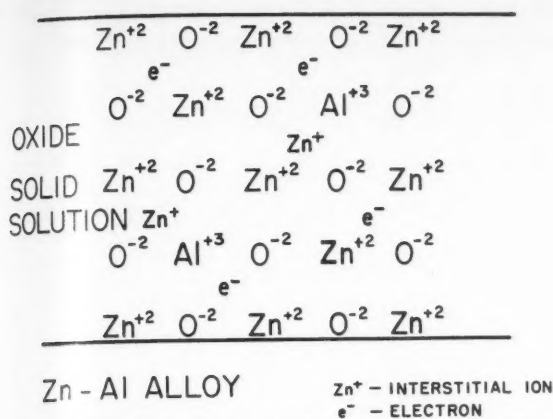
Figure 12—Oxide solid solution formation on zinc-aluminum alloy.[51]

Figure 13—Oxide film model to describe initiation of aqueous corrosion.[57]

of oxides on oxidation rates of alloys is of importance, but as yet little precise experimental information is available.

4. Intramolecular Oxides

The oxidation resistance of a metal may be improved by the formation of a double oxide if the diffusion rates of ions through these structures are decreased. Double oxides generally possess a spinel crystalline structure through which diffusion rates of ions are low. However, the double oxide may not be present in pure form and resistance to oxidation is determined by the combined effect of several phases.

Investigations have been carried out on the formation of double oxides with alumina to determine relative cation diffusion rates.[53, 54] The reaction rates with oxides of zinc, nickel and cobalt are too slow—even to temperature of 1200 C—which indicates that alumina spinels should yield a high degree of protection to a metal against oxidation. This has been verified in practice by the formation of aluminates on nickel.[55]

Dry Oxidation and Wet Corrosion

The role of the oxide film in aqueous corrosion has been neglected until fairly recent years in favor of studies of the electrochemical reactions taking place. In 1951, Evans[56] introduced concepts of the role of oxide films in electrochemical corrosion mechanisms which subsequently have been placed on a qualitative basis.[52, 57-59] The initiation of corrosion in an aqueous environment may be controlled by the relative ease with which cations and electrons pass through the air-formed oxide film with which the metal entered the solution. Although cations and electrons may migrate by lattice defects, this does not imply that the rate of corrosion will follow rate laws governing oxide film formation. Rather, the diffusion mechanism of oxidation operates at low temperatures only during the initiation of corrosion at local areas. These areas of attack occur where the film is thin or where there is a large concentration of lattice defects due to metal impurities or alloying constituents.
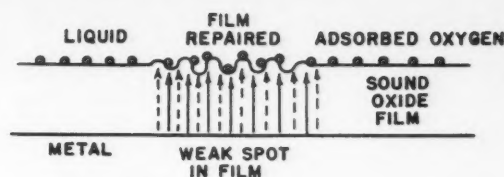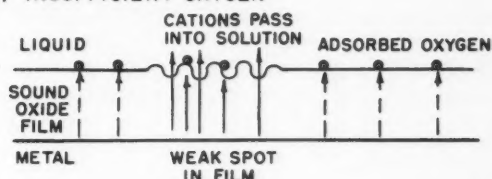
Film and electrochemical theories lead to the same explanation of the corrosion mechanism. As illustrated in Figure 13, cations diffuse via lattice defects at weak areas in the film and electrons diffuse either through the weak areas or through the surrounding oxide film. Figure 13a shows that in the first instance cations and electrons react with adsorbed oxygen at the weak areas and the film tends to heal itself by the formation of additional oxide. In the second instance, some cations enter into solution, Figure 13b, if the supply of oxygen is insufficient to react with all emergent cations. Concurrently, electrons diffuse through the oxide film around the weak area to form oxygen ions with adsorbed oxygen which then pass into solution as hydroxyl ions. Thus, an oxide film model is applicable to the description of electrochemical corrosion as the diffusion of metallic ions at the weak areas represents the anodic reaction and the diffusion of electrons through the oxide film represents the cathodic reaction.

This model may prove useful for the selection of alloying constituents for the prevention of corrosion of metals. Detailed calculations, based on defect structure of the oxide film, have been attempted to determine the role of the surface film in the corrosion of silver in bromine-potassium bromide solutions and the passivity of iron in nitric acid.[52, 59] Also, qualitative concepts of the theory of oxide film formation have been applied to explain the corrosion characteristics of aluminum in aqueous solutions.[57, 58]

The amorphous oxide film on aluminum transmits electrons with difficulty, but more readily than it transmits ions because of the relatively high potential barriers against electron and ion diffusion (Table 3). This confines the anodic reaction to areas where oxide is largely absent and the cathodic reaction to areas where the film is thin. If the oxide film is made a better electronic conductor, the high resistance of aluminum to corrosion will be decreased and the solution potential will be more positive due to an increase in the cathodic area and a decrease in the slope of the cathodic polarization curve. This occurs

if impurities of copper or iron are present in the metal; these metal-deficit oxides, which possess higher electrical conductivities than alumina, are heterogeneously dispersed in the oxide film. Consequently, unalloyed aluminum will be anodic towards aluminum alloys containing copper, which may account for the protection of these alloys in cases where they are clad with high purity aluminum.

Summary

Different models of oxide films have been described which are used to interpret the oxidation characteristics of metals and alloys. For pure metals, the theory advanced to explain the formation of compact films with lattice defects is fairly well developed. The oxidation of aluminum was chosen as an example to illustrate the applicability and limitations of this theory. For alloys, the present state of the theory is unable, because of their complex behavior, to give quantitative interpretation of the phenomena. However, broad principles have been formulated for the selection of alloying elements to prevent deterioration of metals by oxidation. To illustrate these principles, the effect of aluminum as an alloying element has been discussed. Attention also has been given to the role of the oxide film in aqueous corrosion. This review shows that extensive research is required to elucidate further the behavior of oxide films in oxidation and corrosion.

References

1. G. Tammann. *Z. Anorg. u. allgem. Chem.*, **111**, 78 (1920).
2. N. B. Pilling and R. E. Bedworth. *J. Inst. Metals*, **29**, 529 (1923).
3. C. Wagner. *Z. Phys. Chem.* **B21**, 25 (1933).
4. C. Wagner. Atom Movements, ASM, Page 153 (1951).
5. E. A. Gulbransen and K. F. Andrew. *J. Electrochem. Soc.*, **101**, 128 (1954).
6. E. A. Gulbransen. *Annals New York Academy of Sciences*, **58**, 721 (1954).
7. E. A. Gulbransen. *Trans. Electrochem. Soc.*, **83**, 301 (1943).
8. E. A. Gulbransen. Proceedings of the Gothenburg Conference on Solid State Reactions 1952 Gothenburg, Sweden.
9. W. J. Moore. *J. Electrochem. Soc.*, **100**, 302 (1953).
10. N. F. Mott. *Trans. Faraday Soc.*, **36**, 472 (1940).
11. N. Cabrera and N. F. Mott. *Repts. Prog. Phys.* **12**, 163 (1949).
12. U. R. Evans. Symposium on Internal Stresses in Metal Alloys, Inst. Met. (1947).
13. P. D. Dankov and P. V. Churaev. *Doklady Akad. Nauk. SSSR*, **73**, 1221 (1950).
14. U. R. Evans. *Trans. Faraday Soc.*, **41**, 365 (1945).
15. U. R. Evans. *Trans. Am. Inst. Mining Met. Eng.*, **166**, 292 (1946).
16. W. McKewan and W. M. Fassell, Jr. Institute for the Study of Rate Processes, Univ. of Utah, Feb. 1, 1952. AECU 1918, Technical Rep. No. 7.
17. D. E. Davies, U. R. Evans and J. N. Agar. *Proc. Roy. Soc.*, **225A**, 443 (1954).
18. E. A. Gulbransen and W. S. Wysong. *J. Phys. Coll. Chem.*, **51**, 1087 (1947).
19. N. Cabrera. *Phil. Mag.* **40**, 175 (1949).
20. N. Cabrera. *Rev. Met.*, **45**, 86 (1948).
21. N. Cabrera, J. Terrien and J. Hamon. *Compt. rend.*, **224**, 1558 (1947).
22. N. Cabrera and J. Hamon. *Compt. rend.*, **225**, 59 (1947).
23. N. Cabrera. *Rev. Met.*, **45**, 86 (1948).
24. A. Charlesby. *Proc. Phys. Soc.* (London), **66**, 317 (1953).
25. A. Charlesby. *Proc. Phys. Soc.* (London), **66**, 533 (1953).
26. F. Keller and J. D. Edwards. *Metal Progress*, **54**, 35 (1948).
27. N. K. Andrushenko and P. D. Dankov. *C. R. Acad. Sci. URSS*, **62**, 353 (1948).
28. J. Herenguel and J. Boghen. *Rev. Met.*, **51**, 265 (1954).
29. J. M. Cowley. *Acta. Cryst.*, **6**, 846 (1953).
30. R. A. Harrington and R. H. Nelson. *Trans. Am. Inst. Mining Met. Eng.*, **137**, 62 (1940).
31. G. Hass. *Optik*, **1**, 134 (1946).
32. L. De. Brouckère. *J. Inst. Metals*, **71**, 131 (1945).
33. H. G. F. Wilsdorf. *Nature*, **168**, 600 (1951).
34. G. D. Preston and L. L. Bircumshaw. *Phil. Mag.*, **22**, 654 (1936).
35. L. E. Price and G. J. Thomas. *J. Inst. Metals*, **63**, 21, 29 (1938).
36. D. Watanabe, S. Ogawa and T. Kemua. *J. Japan Inst. Metals*, **17**, 108 (1953).
37. C. R. Cupp. *Prog. Met. Phys.*, **4**, 105 (1953).
38. J. L. Meijering. Pittsburgh International Conference on Surface Reactions (1948).
39. E. V. Rhines. Atom Movements ASM, Page 174 (1950).
40. I. A. Makolkin. *Zhur. Priklad. Khim.* USSR, **24**, 460 (1951).
41. A. J. Swain. *J. Inst. Metals*, **80**, 125 (1951).
42. M. Whitaker and A. R. Heath. *J. Inst. Metals*, **82**, 107 (1953).
43. T. E. Leontis and F. N. Rhines. *Trans. Am. Inst. Mining Met. Eng.*, **166**, 265 (1946).
44. R. Eborall and C. E. Ransley. *J. Inst. Metals*, **71**, 525 (1945).
45. E. H. Dix and F. Keller. *Trans. Am. Inst. Mining Met. Eng.*, **1929**, 351.
46. S. Dobinski and M. Niesluchowski. *Nature*, **144**, 510 (1939).
47. P. T. Stroup. Controlled Atmospheres, ASM, (1941).
48. E. A. Smith, Jr. *Light Metal Age*, 24 (Oct. 1954).
49. C. Wagner and K. E. Zimens. *Acta. Chem. Scand.* **1**, 547 (1947).
50. C. Wagner. Pittsburgh International Conference on Surface Reactions (1948).
51. K. Hauffe. *Prog. Met. Phys.*, **4**, 71 (1953).
52. K. Hauffe. *Zeitschrift fur Metallkunde*, **44**, 576 (1954).
53. K. Hauffe and K. Pschera. *Z. anorg. Chem.*, **262**, 147 (1950).
54. B. Bengton and R. Jagitsch. *Ark. Kemi. Min. Geol.*, **24A**, No. 18 (1947).
55. J. Moreau and J. Benard. *Compt. rend.*, **237**, 1417 (1953).
56. U. R. Evans. *Nature*, **168**, 853 (1951).
57. T. P. Hoar and U. R. Evans. *J. Electrochem. Soc.*, **99**, 212 (1952).
58. U. R. Evans. *Trans. Inst. Met. Finishing*, **31**, Advance Copy No. 8 (1954).
59. K. Hauffe. *Werkstoffe und Korrosion*, **3**, 117 (1955).

Any discussions of this article not published above will appear in the December, 1955 issue.

The Porosity of the Aluminum Surface Investigated by the Repetitive Oscillographic Method*

By W. MACHU, E. M. KHAIRY and M. K. HUSSEIN*

Introduction

IN PREVIOUS publications two of the authors investigated the anodic passivity of aluminum in sulfuric acid, sodium sulfate and sodium hydroxide solutions.[1] It was inferred that because of the great affinity of the metal towards oxidation, a more or less passive oxide layer persists on its surface. The porosity of such a layer amounts to ~ 10^{-4} cm²/cm² of the apparent surface area. Many trials were made to obtain an active surface but only the cathodic pretreatment was effective to a small extent.

In the present study the oscillographic method frequently applied for investigating the anodic behavior of several metals[2] was utilized. The method involves the use of the repetitive current obtained by allowing direct current stabilized by a pentode valve to pass through a thyration valve in conjunction with a condenser. While the condenser is being charged the current passes through the electrolytic cell until the condenser voltage reaches the trip voltage of the thyration valve. The arrangement thereby is short-circuited and the condenser discharges. Simultaneously a quantity of electricity equal to that originally passed flows through the cell in the opposite direction. The process of charge and discharge of condenser eventually will repeat itself very rapidly and consequently the electrochemical changes taking place at the electrode surface are rendered repetitive. It has been found that this treatment effects the activation of the electrode surface to a great extent and hence leads to longer times of passivation which could be measured accurately during the taking up of the respective polarization curves. This affords a means for studying the anodic passivity of aluminum in a variety of electrolytes where the direct anodic or cathodic treatment gives no measurable longer passivation times.

The porosity of the aluminum surface in each electrolyte can be calculated by measuring the times of passivation at different current densities. From the respective porosity values the phenomena underlying the corrosion and the passivation of aluminum in different media can be visualized since the porosity of a layer is the most important item governing these two properties.

Experimental Methods

Passivity experiments were carried out in a variety of electrolytes including buffer solutions of

Abstract

Experiments are reported using a repetitive oscillographic method to investigate the anodic behavior of spectroscopically pure aluminum exposed to a variety of electrolytes including buffer solutions of pH 6, 7 and 8, sulfuric acid and sodium sulfate, nitric acid and sodium nitrate, hydrochloric acid and sodium chloride, acetic acid, oxalic acid and disodium hydrogen phosfate.

The method permits determination of the part of the surface area covered by the passivating layer formed through anodic polarization. Results of tests in various electrolytes are reported.

Authors postulate the repetitive oscillographic method in combination with the direct polarization method provides a means of testing among reactions occurring at a metal anode.
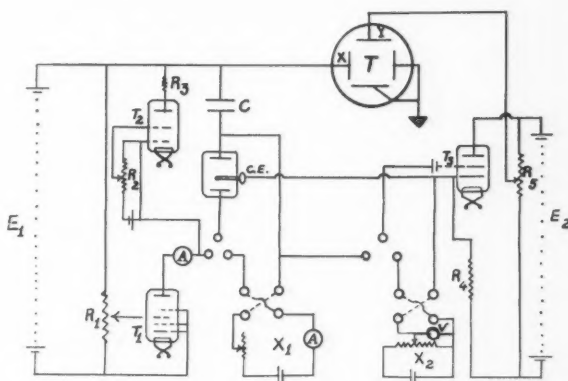
Figure 1—The oscillographic circuit used in experiment.

TABLE 1—Legend for Figure 1

A—Milliameter
C—Variable Condenser
CE—Saturated Calomel Electrode
E_1—Valve Amplifier
E_2—Dry Battery
T—Cathode Ray Tube
T_1—Saturated Pentode Valve
T_2—Thyration Valve
T_3—Amplifier
R_1, R_2, R_3, R_4 & R_5—Potentiometer   Resistances of 15,000, 10,000, 120, 50,000 and 100,000 ohms
V—Voltmeter
X_1—Circuit for Prepolarization of the Electrodes
X_2—Circuit for Drawing the References Lines

pH 6, 7 and 8, sulfuric acid and sodium sulfate, nitric acid and sodium nitrate, hydrochloric acid and sodium chloride, acetic acid, oxalic acid and disodium hydrogen phosfate. Spectroscopically pure rods provided by Johnson and Matthey (London) were used as anode and a platinum wire as cathode. The oscillographic circuit used is essentially the same as that
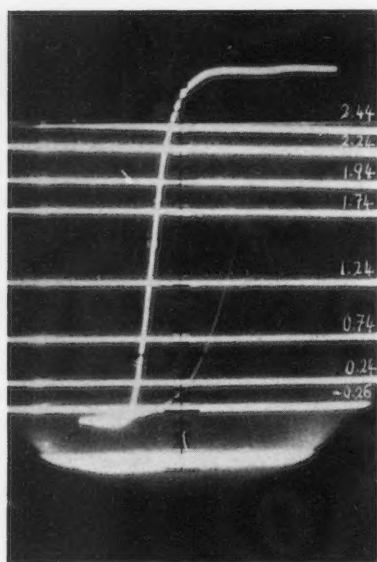
Figure 2—Oscillogram obtained with an aluminum electrode in normal sodium acid phosfate.
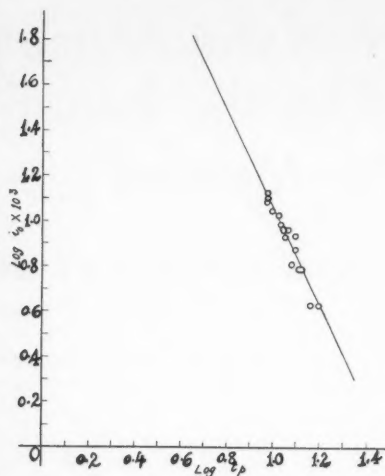
Figure 3—Graph of log current densities (i_o) plotted against log time of passivation (t_p).

TABLE 2—Results Obtained in Various Electrolytes

Electrolytes	Log B_1	B_1	F_o-F%
N H_2SO_4	0.23	1.7	6.5
N Na_2SO_4	0.123	1.3	3.5
0.0025N HCl	0.223	1.7	6.5
0.01N NaCl	0.345	2.2	12.4
2N Na_2HPO_4	0.00	1.0	1.8
N Na_2HPO_4	0.0053	1.01	1.8
0.5N Na_2HPO_4	0.3162	0.48	0.3
0.01N HNO_3	0.549	3.5	37.3
0.005N HNO_3	0.169	1.48	4.6
0.01N $NaNO_3$	0.750	5.6	100.0
0.1N $(COOH)_2$	0.730	5.4	100.0
0.1N CH_3COOH	0.715	5.2	100.0
Potassium acid-phthalate-NaOH buffer pH 6.08	0.730	5.4	100.0
Potassium acid-phthalate-NaOH buffer pH 6.86	0.108	1.3	3.3
Potassium acid-phosfate-NaOH buffer pH 7.9	0.643	4.4	61.0

B = 5.4   n = 0.42

previously applied by Hickling[2] with some modifications. It involves the use of a thyration valve (General Telephone and Cables 3 v/420 BF), a valve amplifier (General Electric 43-C2) in combination with a Cossor cathode ray tube (Model No. 1035) successively in place of the Osram valves (G T I C) and triode MH4 and the gas focussed tube (4050 BB) used by that author (Figure 1 and Table 1).

Results and Discussion

The oscillograms obtained with the aluminum electrode in the different investigated media have the same general shape. From the representative curve taken in normal sodium acid phosfate (Figure 2), it can be seen that aluminum is rendered passive by the time the double layer is built up, a criterion of the existence of a more or less natural passive oxide film. The time of passivation (t_p) is therefore measured at different current densities (i_o) as the time lapse from the moment of switching on the current up to the attainment of passivity as indicated by the sudden potential jump taking place prior to oxygen evolution. Taking F_o and F as representing the total and the covered surface area, respectively, the porosity of the surface (F_o — F) is calculated by the use of the formula:[3]

$$t_p = B \left(\frac{i_o}{F_o - F} \right)^{-n}$$

in which B and n are constants and (F_o — F) denotes the available part of the surface on which the passivating layer is anodically formed. This may or may not be equal to the porosity of the initially present oxide layer depending on the extent of attack exerted by the respective electrolyte during the anodic treatment under the prevailing experimental conditions.

By plotting log i_o against log t_p a straight line is always obtained. Its slope gives the constant n and the intersection with log t_p axis yields the specific time of passivation B_1 (a representative curve is shown in Figure 3). B_1 is always smaller than B but becomes equal to it when the surface initially is completely free. In the present investigation the constant B amounts to 5.4 seconds taken as the maximum B_1 value obtained in the different electrolytes. The porosity F_o — F is given by the derived equation:[4]

$$\log (F_o - F) = \frac{\log B_1 - \log B}{n}$$

It should be noted that the value of F_o — F = 100 corresponds to the total area likely to be covered with the passive film irrespective of the initially present layer which under such conditions either must be destroyed or take some part in the process of film formation.

Table 2 contains the results obtained in all investigated electrolytes. From these data the following things can be seen:

a) *Reactions Involved.*

The maximum B_1 value amounting to 5.4 sec/amp/ cm^2 is attained in 0.01 N sodium nitrate, 0.1 N oxalic acid, 0.1 N acetic acid and potassium acid phthalate—NaOH buffer of pH 6. It is considered as the specific time of passivation B corresponding to F_o — F = 100 percent. The anodic behavior in such electrolytes may be explained by assuming that the natural oxide film is attacked by the anions during the anodic polarization yielding the respective easily soluble aluminum salts. These are readily hydrolyzed yielding the hydroxide which covers the whole surface, rendering it passive. Hydrolysis is revealed by the appearance of a gelatinous precipitate on the electrode surface attaining sometimes an appreciable thickness.

Two types of reactions supposedly occur at the electrode surface: An electrochemical reaction and a chemical one which results in the formation of aluminum hydroxide in the vicinity of the electrode

surface. [...] immersi[...] nitrate, [...] layer is [...] adsorptio[...] anions w[...] the vicin[...] by anodi[...] layer as[...] interact [...] the elect[...] of the sli[...]

It sho[...] oxidatio[...] bare met[...] competi[...] chemica[...] method. [...] surface, [...] oxidatio[...] process [...] sivity is [...] duced h[...] the who[...] passivity[...] mation [...] the ulti[...] layer (r[...] be total[...] come re[...] 0.01 N r[...] aluminu[...] face oxi[...] relativel[...] ing laye[...] the prim[...]

b) *Hydr[...]*

The r[...] fate mec[...] pH 7.9, [...] those ob[...] pH 7 ([...] tained a[...] great pa[...] hydroxi[...] solution[...] sivating [...] the ava[...] parent [...] tions of [...] layer is [...] tion (0.[...] about 2[...] tions. A[...] respecti[...] chemica[...] At pH [...] be hydr[...] centrati[...]

c) *Activ[...]*

The b[...] reveals

surface. This may be visualized by assuming that on immersing the electrode in media containing chloride, nitrate, oxalate or acetate anions, the natural oxide layer is virtually attacked through preferential adsorption and/or penetration of the respective anions which are present in a greater prepondrance in the vicinity of the anode surface. Metal ions released by anodic dissolution through the pores of the oxide layer as well as those produced by anionic attack interact with the hydroxyl ions migrating towards the electrode surface. This leads to the precipitation of the slightly soluble aluminum hydroxide.

It should be recognized that the electrochemical oxidation of aluminum through the interaction of the bare metal parts with the discharged hydroxyl ions is competing simultaneously with the above described chemical reaction. The application of the repetitive method, being a means for activating the electrode surface, affects the suppresion of the electrochemical oxidation process to such an extent that the chemical process predominates. Under such conditions passivity is brought about through a chemically-produced hydroxide layer covering, in the extreme case, the whole electrode surface. It could happen that passivity would be brought about through the formation of a secondary layer (hydroxide) covering, in the ultimate case, the whole surface of the primary layer (natural) and not necessarily that the latter be totally destroyed in order that the surface become relatively 100 percent porous. Accordingly in 0.01 N nitric acid (which has a dissolving action on aluminum hydroxide) the anionic attack of the surface oxide and the hydrolysis of the formed salt are relatively hampered in such a way that the passivating layer covers only 37 percent of the surface of the primary layer.

b) Hydroxide and Phosfate Ions

The maximum $F_o — F$ value attained in the phosfate media amounts to 61 percent of the surface at pH 7.9, a value which is very much greater than those obtained in sodium phosfate solutions or at pH 7 (from 0.3-3 percent). The high porosity obtained at pH 7.9 may be attributed to the attack of a great part of the initially present oxide layer through hydroxide ions. Since aluminum oxide is stable in solutions within the pH range 5-7, the anodic passivating layers can form only in such media within the available pores on the metal surface. It is apparent that in disodium hydrogen phosfate solutions of concentrations lower than 1 N, the phosfate layer is formed which covers only a very small fraction (0.3 percent) of the surface as compared with about 2 percent area covered at higher concentrations. At the same time 99.7 percent and 99 percent respectively of the total surface are covered by chemically formed aluminum salt (e.g. hydroxide). At pH 7 the anodically formed layer is more like to be hydroxide than phosfate owing to the small concentration of the phosfate ion (0.05 M).

c) Activating Effect of Chloride Ion.

The behavior of aluminum anodes in chloride media reveals the great activating effect of the chloride ion,

passivity being achieved only at concentrations smaller than 0.01 N. At higher concentrations the potential remains at a pronounced negative value and the underlying anodic process is merely the dissolution of the metal. As can be seen from Table 2 the chloride ion still manifests its activating effect in solutions as dilute as 0.0025 N ; the porosity amounts to 12 percent in 0.01 N NaCl and to ~ 7 percent in the 0.0025 N HCl.

The role of this ion is further substantiated by the fact that the activating effect of N H_2SO_4 is almost equivalent to that of 0.0025 N HCl. This indicates that the determining factor in this respect is not merely the hydrogen ion concentration but the specific effect of the individual anion as well as the rate of hydrolysis at the surface. This view is supported by the fact that weak acids (acetic and oxalic) or even neutral solutions (sodium nitrate) yielded a greater apparent free surface area than strong acids of appreciable hydrogen ion activities.

From the above results it also can be concluded that electrolytes yielding porosities of less than about 10 percent are suitable for anodizing aluminum irrespective of the activating effect furnished by the repetitive nature of the process. It is thought that the electrochemical oxidation overbalances the dissolution effect of the electrolyte. Alternatively electrolytes which are characterized by a 100 percent free surface area apparently are unsuitable for anodizing properties. Through local action it may happen in these solutions that the natural oxide layer is easily destroyed, under which conditions the electrochemical process is rendered incapable of restoring the passivating oxide film. It may be noted also that the destructive effect manifested by the chloride ions demonstrates their corrosive action and suggests the necessity of their absence from the anodizing bath.

On comparing the results obtained in this investigation with those obtained by the direct method[1] it is obvious that the repetitive nature effects much more pronounced activity. Whereas the maximum porosity achieved by the direct pretreatment amounts to ~ 10^{-3} cm^2/cm^2 of the apparent surface area, a 100 percent activation is approached by applying the repetitive method even at lower current densities. The effect of superimposed AC and DC currents in bringing about activation and thus the dissolution of gold anodes in the well known Wohlwill-process may be recalled in this respect.

The results obtained in this investigation show that information obtained by the application of the oscillographic method together with that obtained by the direct anodic treatment makes it possible to distinguish the different types of reactions which may take place at the metal anode. By doing this a further insight into the anodic behavior of different metals under a variety of conditions becomes possible.

Summary

1. The repetitive method was applied for studying the anodic passivity of aluminum in a variety of electrolytes including buffer solutions of pH 6-8, sulfuric acid and sodium sulfate, nitric acid and sodium nitrate, hydrochloric acid and sodium chlo-

ride, acetic acid, oxalic acid and disodium hydrogen phosfate. Experiments were carried out at different current densities and the respective times of passivation were measured during the taking up of the curves.

2. The porosity of the aluminum surface was calculated in the above electrolytes. The results obtained showed that two types of reactions occur: Electrochemical and chemical. The former leads to the oxidation of the metal and the latter involves anionic attack with the formation of the respective salts. Hydrolysis may take place under certain conditions resulting in an increase of the initial porosity of the surface. The maximum porosity corresponding to the free state of the surface was achieved in sodium nitrate, oxalic acid, acetic acid and buffer of pH 6.

3. The anodic behavior in chloride media revealed the great activating effect of the chloride ion at con-

centrations higher than 0.01 N. In sodium phosfate solutions, however, the natural oxide persisted and the passivating layer was formed mainly in the available pores on the surface.

4. The repetitive oscillographic method in combination with the direct polarization method provided a means for distinguishing the different types of reactions occurring at a metal anode.

References

1. W. Machu and M. Kamal Hussein. *Werkstoffe und Korrosion*, **5**, 49 (1954); *ibid.*, **5**, 295 (1954).
2. A. Hickling. *Trans. Faraday Soc.*, **41**, 333 (1945), *ibid.*, **42**, 518 (1946); A. Levin and V. Sotnikova, *J. Gen. Chem. Russ.*, **13**, 661 (1943); A. Riad Tourky, E. M. Khairy and M. K. Hussein, The Anodic Behaviour of Aluminum (in the course of publication).
3. W. J. Müller. Die Bedekungstheorie der Passivität (Berlin, 1933) Verlag Chemie.
4. W. Machu and E. M. Khairy. *Werkstoffe und Korrosion*, **5**, 11 (1954).

*Any discussions of this article not published above
will appear in the December, 1955 issue.*

TECHNICAL PAPERS ON CORROSION WELCOMED

Authors of technical papers on corrosion are invited to submit them for review without invitation to the Editor of Corrosion. Write for "Guide for the Preparation and Presentation of Papers" sent free on request to prospective authors.

Corrosion of Materials Subjected to Locomotive Smoke and Funnel Blast*

By T. MARSHALL* and R. M. SINCLAIR**

Introduction

IN CONTRAST to American "round-house" practice, locomotive maintenance sheds in New Zealand are built over sections of railway line to house parallel rows of locomotives. A typical shed, for example, houses three rows of locomotives and measures approximately 300 x 60 feet.

In sheds housing coal-burning or oil-burning locomotives rapid smoke extraction is essential for the comfort and efficiency of maintenance crews. Experience has demonstrated the inadequacy of simple roof louvers. Present practice is to use long, inverted U-ducts (about 5 x 5 feet in section) suspended over the rows of locomotive funnels to remove smoke to vertical stacks built at intervals along the ducts and extending through the roof. Smoke extraction via the ducts and stacks usually depends on natural convection but may be assisted mechanically.

Desirable Properties

Experience has shown the following properties are essential for materials used in construction of smoke ducts:

1. The materials must be resistant to deterioration in the highly corrosive atmosphere contaminated with steam, smoke, sulfurous fumes, fly-ash and soot. It has been found that common structural materials such as mild steel and galvanized steel show rapid corrosion when so exposed.
2. A fairly high strength/weight ratio is desirable to minimize the weight and cost of structures supporting the ducts. For this reason relatively thin sheet metal is advantageous for duct construction.
3. Materials and structures must be capable of withstanding direct funnel blast from locomotives at distances of four feet or less. Brittle materials therefore must be avoided. It was found, for example, that ¼-inch asbestos-cement panels in smoke-duct service failed to withstand funnel blast.
4. Fire-resistant materials are essential. Timber structures are avoided for obvious reasons although small quantities of hardwood or other combustible materials are employed occasionally.
5. Materials must give a maintenance-free service life of at least 20 years. Owing to gross contamination with tarry soot deposits and to labor conditions, structures are not given regular periodic maintenance.
6. The material must be such that costs can be kept to a minimum when balanced against effective service life.

None of the structural materials used to date (mild steel, galvanized steel, asbestos cement sheet) have been considered satisfactory in smoke-duct service.

Tests were conducted to assess the relative cor-

Abstract

A description is given of tests on various constructional materials and protective coatings exposed to smoke, steam and direct funnel blast from coal-burning and oil-burning locomotives. Results indicate that molybdenum-bearing austenitic stainless steel and vitreous-enamelled steel are highly resistant to deterioration in this severely corrosive environment.

rosion resistances of a number of materials and protective systems (see Tables 1-5). Several materials used previously and found unsuitable were included in the tests for comparison purposes.

Apart from the immediate purpose of improving smoke-duct design, the tests give a useful indication of the behavior of materials and protective coatings in other sheltered environments exposed to locomotive smoke and steam. Examples of this include tunnels and the undersides of overhead bridges. It must be stressed however, that the tests do not indicate the relative behavior of materials in smoke-polluted atmospheres which are simultaneously exposed to the weather and to the washing action of rain. For example, they do not apply to external surfaces of locomotive-shed roofs.

Materials Tested

Non-metallic materials and protective systems used in the tests are listed below in Tables 3-5 with brief appendices on their compositions. It will be noted that many thick-film, plastic-type surface coatings of potentially high protective value were not included, such omissions being made because of fire hazards, high costs and limited availability in New Zealand.

All materials were tested in the form and surface condition most likely to apply in actual smoke-duct constructions (for example flat or corrugated sheet).

Compositions of the unprotected alloys tested are given in Table 1. All these alloys were exposed in the form of bright-surfaced sheet, cold-rolled (except in the case of "Alclad" and galvanized steel) and with the stainless steels polished on one surface. Sheets varied in thickness from .030 to .068-inch.

Test Procedure

Rectangular panels of materials to be tested were mounted on a hardwood frame. The frame was then suspended, with the panel surfaces horizontal, inside the existing smoke duct of a shed used continuously by coal-burning and oil-burning locomotives. This form of panel mounting was adopted to closely simulate service exposure by subjecting panel surfaces to the full funnel-blast of locomotives and to indi-

TABLE 1—Analyses of Alloys Tested

ALLOY	Nearest Equivalent American Specification	Percent Composition (R=Remainder, Max.=Maximum, Min.=Minimum)																	Remarks
		C	S	P	Si	Mn	Mg	Fe	Cu	Ni	Cr	Mo	Ti	Nb	Al	Bi	Sn	As	
Mild Steel	AISI C1006	0.06	0.04	0.02	0.04	0.3	..	R	0.1	0.05	0.01	..	..	..	..	..	..	..	
18/8 Cr Ni Stainless Steel	AISI 301	..	..	..	0.4	0.5	..	R	0.15	9	19	0.01	0.02	0.05	..	..	..	..	Non-stabilized
18/8/3 Cr Ni Mo Stainless Steel	AISI 316	0.05	..	0.03	0.3	0.29	..	R	0.3	7.9	17.6	3.16	0.02 Max.	..	..	..	..	..	Non-stabilized
Copper	SAE 71 Type A	..	..	..	..	..	..	0.01	R	0.005	..	..	..	..	..	0.002	0.005	0.02	Commercial tough pitch copper
Aluminum	Alcoa 2S-H	..	..	..	0.15	0.01	0.01	0.47	0.11	..	..	..	..	..	R	..	..	..	
Aluminum Manganese Alloy	Alcoa 3S-H	..	..	..	0.1	1.1	0.01	0.35	0.05	..	..	..	..	..	R	..	..	..	
Aluminum-Magnesium Alloy	Alcan 57S	..	..	..	0.15	0.32	1.65	0.29	0.01	..	..	..	..	..	R	..	..	..	Birmabright Specification BB2
Clad Aluminum Alloy[1] (core composition)	Alcoa Alclad 24S-T4	..	..	..	0.7 Max.	0.3/1.2	0.6/1.8	0.7 Max.	3.5/5.0	..	..	..	..	..	R	..	..	..	Specification analysis to DTD 390. Cladding composition Al-99.5 percent Min
Galvanized Steel	....	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	Commercial hot-dip galvanized steel sheet

[1] In the solution-treated and room-temperature aged condition. Sheet of total thickness .031-inch, cladding layers each 5 percent of total thickness.

TABLE 2—Test Results for Unprotected Alloys

Alloy	Exposure Time (Years)	Average Corrosion Rate (Mils per Year)	Nature of Corrosion Product	Type of Attack
Mild Steel	1.7	8	Laminar rust	General*
18/8 Cr Ni Stainless Steel	1.0	1	Adherent rust	Very numerous, shallow pits
18/8/3 Cr Ni Mo Stainless Steel	1.7	0.1	A few rust spots	Very slight, shallow pitting
Copper	1.0	2	Adherent oxide film	Even, general
Aluminum	1.0	5	Non-adherent oxide scale	Severe pitting and moderate general attack
Aluminum-Manganese Alloy	1.0	3	Non-adherent oxide scale	Severe pitting and moderate general attack
Aluminum-Magnesium Alloy	1.0	3	Non-adherent oxide scale	Severe pitting with numerous very deep local pits and moderate general attack
Clad Aluminum Alloy	1.0	2	Non-adherent oxide scale	Cladding stripped. Uneven, deep pitting in core alloy plus moderate general attack
Galvanized Steel	1.0	—	Adherent rust	Severe. Zinc coating stripped. Shallow pitting of the underlying steel

* The term 'general' is used to indicate attack over the entire test surface area.

cate differences between corrosion rates on upper and lower surfaces. Corrosion on upper surfaces proved to be slightly but not significantly less severe than on under surfaces of the panels.

Exposure periods varied from 0.7 to 3 years but were in all cases long enough to give results indicative of long-term behavior.

Panels of unprotected alloys were used in various sizes, each with a total surface area of not less than one sq. dm. (15 square inches). Test methods and determinations of average corrosion rates followed the ASTM recommended procedure,[1] with cleaning methods as described by Uhlig.[2]

Non-metallic materials also were exposed as panels, each with a total surface area not less than four sq. dm. Weighing the cleaned panels before and after test permitted assessment of any gain or loss of weight during exposure. Panels also were subjected to visual examination for surface deterioration, softening and cracking.

Test procedure for protective coating systems followed a similar pattern. The coatings were applied to clean steel or aluminum panels each with a total

TABLE 3—Test Results for Protective Coatings (Other than Paints) on Steel

Protective Coating[1]	Exposure Time (Years)	Effect of Exposure on Coating
Proprietary bituminous coating[2]	1.0	Bituminous coating sagged away from underside of steel.
Vulcanized rubber[3]	1.7	No visible deterioration.
Proprietary zinc-dust baked coating[4]	1.7	Coating stripped after 0.5 years exposure; severe rusting on underlying steel.
Vitreous enamel[5]	1.0	Face carrying ground coat only showed local penetration at numerous points, allowing local rusting of steel. No lateral rusting beneath enamel. Face carrying ground coat plus finishing coat showed no penetration and no visible deterioration. Gloss still remained on finishing coat.
Vitreous enamel[6] (high-titania variety)	1.0	No significant weight loss and no visible deterioration of enamel. Gloss still remained on finishing coat.

[1] Coatings all applied to steel.
[2] Bitumen-impregnated fabric on corrugated black steel sheet.
[3] Rubber coatings (0.05-inch thickness) vulcanized on to the surfaces of flat steel sheet.
[4] Baked coating of the zinc dust-sodium silicate type on mild-steel plate.
[5] Vitreous enamel of the type commonly used on kitchen ware. Ground coat only on one side, ground coat and white finishing coat on the other side.
[6] A high-titania vitreous enamel specially formulated for heat resistance. Ground coat and finishing coat on each side of panel.

TABLE 4—Test Results for Paint Coatings

Paint System on Panel	Panel Alloy	Exposure Time (Years)	Condition of Paint Film After Exposure
One chromate priming coat[3] + two aluminum finishing coats[1]	Aluminum[2]	1.7	Numerous small blisters on under surface with a few small blisters on upper surface; remainder of film intact except for severe blistering and film rupture at edges.
One chromate priming coat[3] + two aluminum finishing coats[1]	Aluminum[2] with M.B.V. surface treatment[4]	1.7	A few small blisters on under surface; film intact on upper surface with moderate film breakdown at edges of panel.
Three coats of aluminum-pigmented bituminous paint	Aluminum[2]	1.7	Film breakdown at numerous points on under surface with lateral corrosion of metal beneath the film. Similar, but less severe breakdown of film on upper surface of panel.
Three coats of aluminum-pigmented silicone-alkyd heat-resisting paint	Aluminum[7]	1.2	Film embrittled, flaked off 30 percent of under surface and flaked off in small patches from upper surface of panel. Corrosion occurring on the bared metal.
One chromate priming coat[3] + two aluminum finishing coats[1]	Mild steel, pickled by Footner duplex process[5]	1.7	Film breakdown at four points on under surface, at one point on upper surface, and partial breakdown along panel edges. Rust nodules and pitting of underlying steel at points of breakdown.
One chromate priming coat[3] + two aluminum finishing coats[1]	Mild steel, 'Bonderized'[6]	1.7	Film breakdown at 12 points on under surface, at two points on upper surface and partial breakdown at panel edges. Rust nodules at points of film rupture.
Three coats of aluminum-pigmented bituminous paint	Mild steel, pickled by Footner duplex process[5]	1.7	Film stripped from 50 percent of under surface, leaving bare, severely-rusted steel. Similar but slightly less severe breakdown of film on upper surface of panel.
Three coats of asbestos-filled bituminous paint	Mild steel, pickled by Footner duplex process[5]	1.7	On both panel surfaces a superficial, hard, blistered skin had formed over an underlying plastic layer of the coating adhering to the steel. Complete rupture of the film at edges permitted rusting of steel to ¼ inch in from the panel borders.
Three coats of chlorinated-rubber paint	Mild steel, pickled by Footner duplex process[5]	1.7	Severe blistering and flaking of film with accompanying rusting of steel on both surfaces of panel.

[1] Aluminum-pigmented 100 percent phenolic-tung-linseed varnish.
[2] To Alcoa specification 3S ½H.
[3] Zinc-chromate-pigmented 100 percent phenolic-tung-linseed varnish.
[4] A chemical surface-treatment involving immersion in a hot, alkaline chromate bath.
[5] Five percent sulfuric acid at 80 C followed by 2 percent phosphoric acid (containing 0.5 percent of iron) at 80 C.
[6] A proprietary hot-process phosphate surface-treatment.
[7] Alcoa specification 2S H.

surface area of not less than four sq. dm. The panels then were exposed in the smoke duct, cleaned by scrubbing lightly in water and examined visually for deterioration.

All panels carried pre-drilled holes to facilitate nailing to the hardwood frame. Damage during mounting was minimized by the use of thick rubber washers beneath nail heads and between panels and frame. Panels were spaced well apart to avoid dissimilar metal contact corrosion, each panel being mounted with nails of closely similar composition. For example, aluminum nails were used on aluminum panels, steel nails on mild-steel and stainless-steel panels and copper nails on copper panels.

Test Results

Test results are summarized together with other relevant details in Tables 1-5. Average corrosion rates are given to one significant figure which is, in all cases, well within the accuracy limits of the method of assessment.

Discussion

Results of these tests correlate well with results of similar tests by H. F. Brown,[3] and S. C. Britton[4] and cover a greater range of non-metallic materials and protective coatings.

Austenitic stainless steels, especially the molybdenum-bearing variety, were highly resistant to corrosion but their high cost is a serious drawback in their use for smoke-duct construction.

All the other unprotected alloys exhibited moderate to poor corrosion resistance. It is well known that in most atmospheric environments the corrosion rates of aluminum alloys decrease with increased

TABLE 5—Summary of Test Results for Non-Metallic Materials

MATERIAL	Exposure Time (Years)	Effect of Exposure
Asbestos-cement sheet[1]	3.0	One test panel was lost as a result of locomotive funnel blast. A second panel showed a slight increase in thickness (3 percent) and a definite gain in weight (9 percent). There was no surface softening or any other visible deterioration. The inherent brittleness of the material resulted in cracks at mounting-bolt holes during exposure.
Resin-bonded fibre board[2]	1.7	The test panel showed a slight (1 percent) gain in weight, however, no softening, crazing or any other obvious deterioration occurred. The inherent brittleness of the material gave trouble by cracking during panel-mounting.

[1] Asbestos fibre bonded with Portland cement, in sheets ¼ inch thick.
[2] A corrugated, Bakelite-resin-bonded fibre type of roofing sheet, ⅛ inch thick.

exposure time, the corrosion being self-stifling due to formation of protective surface films. In this case however, there was no evidence of any significant self-stifling action. Layers of corrosion product repeatedly formed on and broke away from the aluminum alloy surfaces during exposure.

The perfectly even, general form of corrosion on copper is a desirable feature but high cost again is a disadvantage.

The two non-metallic materials showed high resistance to deterioration but both are inherently brittle.

Some of the paint systems in Table 4, especially the chromate primer/aluminum finishing system, gave good protection to the underlying metal for the period of test. The dry film thickness of the chromate primer/aluminum finishing system averaged 2.0 mils and no doubt its protective value could have been enhanced considerably by increasing the thickness to four to five mils. It is obvious, however, that such

systems cannot be relied on for complete protection of metals over periods of 20 years or more without periodic maintenance. Adequate maintenance of paints on tar and soot-coated smoke ducts is completely impractical.

Of the other protective coating systems tested, only vitreous enamels and rubber coatings were resistant to the environment. Because of the fire hazard, rubber coatings are not too well suited for smoke duct service.

Conclusions

The tests showed that vitreous enamelled steel with the normal two-coat enamelling system has the best combination of corrosion resistance, strength/weight ratio, freedom from brittleness, fire resistance and low cost. Vitreous enamelled steel with stainless steel bolts and vulcanized rubber washers therefore is recommended for smoke-duct construction.

The information derived from these tests is considered applicable to equipment exposed in similar sheltered environments, such as tunnels, where severe contamination occurs from locomotive smoke and steam blast.

Acknowledgments

The authors acknowledge the cooperation of the New Zealand Railways Department, the National Electric Engineering Corporation, Davy Sandblasting and Engineering Co., Ltd. and A. S. Patterson Ltd. in providing samples and facilities for these tests. They thank the Director of Dominion Laboratory for permission to publish the test results.

References

1. ASTM Recommended Procedure for the Conducting of Plant Corrosion Tests. ASTM Standards, 1946, Part 1A, Page 491 (A224-46).
2. H. H. Uhlig. Corrosion Handbook, 1948, Page 1081, John Wiley and Sons.
3. Application of Corrosion-Resisting Materials to Railroad Electrical Construction. (Association of American Railroads, Chicago) By H. F. Brown. Digest Published in *Corrosion*, 6, 268 (1950).
4. S. C. Britton. *J. Inst. of Civil Engineers*, 16, 65-72 (1941).

Any discussions of this article not published above will appear in the December, 1955 Issue.

Vol. II

re se-
smoke

of the
tional
blast-
erson
these
bora-

ing of
rt 1A,

, John

ailroad
ilroads,
rrosion,

41).

Atmospheric Galvanic Couple Corrosion*

By K. G. COMPTON, A. MENDIZZA and W. W. BRADLEY

Introduction

GALVANIC COUPLE CORROSION has been studied extensively in sea water and in connection with chemical process equipment. A good general discussion of some of the fundamentals and of specific corrosion tendencies of various metals in sea water is given in the Corrosion Handbook.[1] However, few data of a quantitative nature have been published on the corrosion of samples which have been exposed to the atmosphere. The American Society for Testing Materials[2] has maintained a program of testing couples in the form of discs bolted together and has reported the results from time to time.

In the work reported in this paper an attempt was made to obtain information of a nature that would explain the behavior of couples in the atmosphere and predict their probable relative corrosion behavior. Measurements were made of the galvanic couple corrosion currents and electrode potentials in an arrangement that somewhat simulated an atmospheric exposure and of the weight losses of couples in representative atmospheres.

A second objective of this work was to obtain information which would be useful to the design engineer. Many specifications and articles in the literature[3] warn him of the dangers of galvanic couple corrosion but give little or no data of direct use to him. It is believed that the relative quantitative features of this work will provide a much firmer foundation for design than has been available heretofore.

Potentials and Corrosion Currents

In many discussions of galvanic couple corrosion, reference is made to the electrochemical or electromotive series of metals as usually published in text books. In a few instances tables have been presented of the potentials obtained under an arbitrary set of conditions in such media as sea water or 3 percent sodium chloride solutions. These data are useful in pointing to the source of the driving power in galvanic couple corrosion but they tend to create misconceptions of an oversimplified nature. Data have not been available which emphasize the role of the corrosion currents in any relative and quantitative form. While the studies reported here are also of an arbitrary nature it is believed that they form a basis for comparisons that is somewhat more quantitative than data available in the past.

Various schemes have been considered for making measurements of the galvanic couple corrosion currents and of the potentials associated with couples

Abstract

Tests designed to provide fundamental information explaining the behavior of galvanic couples in the atmosphere are reported. The purpose is to permit prediction of their probable relative behavior. Measurements of weight losses of couples in a marine, an industrial and a severe tropical atmosphere are reported.

Tests involving thin sheet electrode material separated by filter paper saturated with electrolyte are reported. Materials tested include aluminum, magnesium, stainless steel, copper, cadmium, zinc, nickel, tin, chromium, lead electroplate, silver, low carbon steel and others. Potential measurements and weight loss data are given. Specimens exposed to the atmospheres show several apparent weight loss anomalies.

Measurements of corrosion currents described provide a quick means for determining probable relative corrosion behavior of couples. Differences between couples "exposed" and "sheltered" are noted. Quantitative data provided are intended to be useful to the design engineer.

K. G. COMPTON—Has worked with corrosion problems for more than 25 years at the Bell Telephone Laboratories, Murray Hill, N. J. During World War II he was a consultant on the deterioration of materials to the NDRC and the Chief of Ordnance; he has also been active on corrosion committees of several technical societies. It was at the State College of Washington that he received his training in electrical and chemical engineering and in electrochemistry.

A. MENDIZZA—Has been associated with the Bell Telephone Laboratories for the past 26 years. His work has been concerned chiefly with general corrosion problems and with the engineering of metallic finishes for the telephone plant. He received his undergraduate training in chemical engineering at Cooper Union and did work for an AM degree at Columbia University. A member of NACE and the Electrochemical Society, he has also been active in ASTM and AES committee work.

W. W. BRADLEY—Has been with Bell Telephone Laboratories since 1949, working primarily on problems involving corrosion and its mitigation in connection with atmospheric exposures. He was with the Army Air Force Weather Service from 1943 to 1946 and received an MS in Chemical Engineering in 1949 from the University of Colorado. He is a member of the Electrochemical Society.

exposed to the atmosphere. One early experiment consisted in wrapping a fine wire in the threads of a bolt over a separating layer of condenser paper.

Figure 1—Details and assembly of galvanic couples for current and potential measurements.
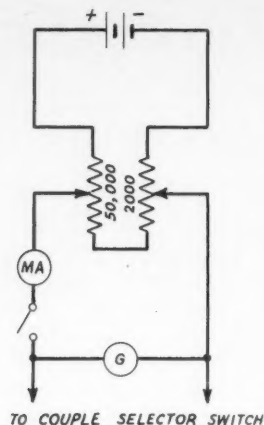
Measurements were made of the potentials when the specimen was exposed to the industrial atmosphere of New York City. Other combinations of electrodes were tried, both exposed to a natural environment and to an artificial one. It soon became evident that several conditions would have to be met if useful data were to be obtained. The amount of moisture present would have to be relatively constant so as to represent a relatively uniform and constant film of the electrolyte bridging the couple junction. The moisture or liquid containing the electrolytic ions should be restrained so that the products produced at the anode and cathode and the concentration effects would be localized. The temperature would have to be controlled and the access of air to the anodic and cathodic surfaces would have to be reproducible from one experiment to another.

Testing Devices

After a number of exploratory experiments, the assembly shown in Figure 1 was selected. Two electrodes of thin sheet material with tabs at one corner and having an area of one square inch were arranged with a sheet of filter paper between them as shown. The backs of the electrodes were shielded by squares of Lucite. This assembly was mounted in the jar in such a way that the lower end of the filter paper dipped into the liquid. The electrolyte reached the couple by capillary wick action and was relatively constant in quantity. A reference electrode could be placed in the liquid for determining the single electrode potentials and also that of the resultant couple when short circuited externally.

Figure 2—Zero resistance circuit for measuring galvanic couple currents.

It was felt that this arrangement would simulate an atmospheric exposure, except for denying ready access of air to the couple. For the purpose of these experiments dilute sea water or sodium chloride can be considered as representative of a marine atmosphere, an acidified dilute solution of sodium sulfate as representative of an industrial atmosphere and distilled water as representative of dew and condensation in the tropics.

The potentials were measured against a silver/silver chloride electrode by means of a potentiometer and the currents were measured by the zero resistance milliameter method[3] shown in Figure 2. A few determinations were made with recording instruments but this was found to be unnecessary. The temperature was controlled by placing the jars in a constant temperature water bath. All determinations were made in quadruplicate.

The materials used in the studies are given in Table 1.

The electrodes were cleaned with solvent and assembled in the fixtures. No effort was made to remove natural oxides or impurities from the surfaces by chemical or mechanical treatments. When the specimens were inserted in the bottles with the "wick" of filter paper dipping in the electrolyte, the assembly was placed in the water bath immediately and a measurement made of the single electrode potentials against the silver chloride reference electrode. This was called an initial measurement but no effort was made to control the time; it was simply a measurement made as quickly as possible after contact with the electrolyte. In some of the early work, measurements of the potentials were made for periods up to 48 hours, but it was found that these had begun to stabilize in most instances after two or three hours. As a standard procedure, the potentials were measured over a two hour period, then the couple was shorted and the galvanic corrosion current was determined by means of the circuit shown in Figure 2.

Both the current and potential of each shorted couple were measured over a period of several thousand minutes (2-3 days). At the end of the period, the couple short circuit was opened and the potentials of the individual electrodes measured again over a "recovery" period of two hours.

Spread and Time Changes

The silver/silver chloride reference electrodes were frequently checked against each other and against a saturated calomel electrode to insure that the electrodes were functioning properly. As was to be expected, a considerable spread was found in the values of the potential of like metal specimens, from specimen to specimen and with time. In some cases the

TABLE 1—Material Used in Tests

Designation	COMPOSITION (Nominal)
Al	2S Aluminum (99.0+Al)
Mg	FS-1 Magensium Alloy (3% Al; 1% Zn; 0.3 Mn; Bal. Mg)
430	430 Stainless Steel (16% Cr; 0.12 C; Bal. Fe)
302	302 Stainless Steel (18% Cr; 9% Ni; 1.25% Mn; .08–.20% C; Bal. Fe)
M	Monel (67% Ni; 30% Cu; 1.4% Fe; 1% Mn; 0.1% Si; 0.15% C)
BR	Brass (59-64.5% Cu; 1.3-2.3% Pb; Bal. Zn)
Cu	Electrolytic Copper (99.9% Cu)
Cd	Cadmium electroplate > 0.001-inch thick on steel
Zn	Zinc electroplate > 0.001-inch thick on steel
Ni	Nickel electroplate > 0.001-inch thick on brass
Sn	Tin electroplate > 0.001-inch thick on steel
Cr	Chromium electroplate > 0.002-inch thick on copper
Pb	Lead electroplate > 0.001-inch thick on steel
Ag	Silver (99.9+Ag)
Fe	Low carbon steel

Figure 3—Potentials and currents of zinc-aluminum couples.

Figure 4—Potentials and currents of iron-430 steel couples.

Figure 5—Potentials and currents of couples of chromium with silver, aluminum and magnesium in 0.01N NaCl.

Figure 6—Statistical chart of the single electrode potentials of several metals.

values became more negative with time and in others more positive or drifted back and forth.

Inasmuch as the measured potentials are the resultants of the potentials of the various small anodic and cathodic areas on the metal surface at any given time, both the spread and changes with time have considerable significance in providing an explanation for the actual behavior of galvanic couple corrosion under service conditions. A typical example is given in Figure 3 where the averages of th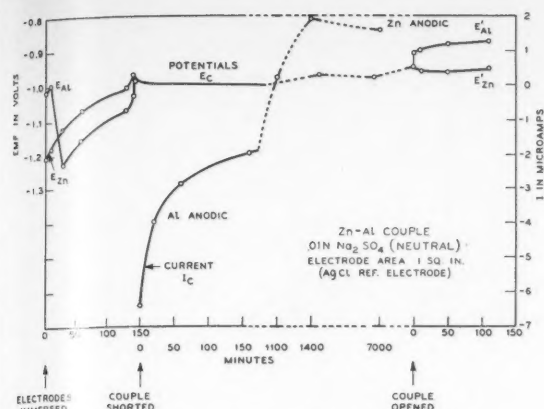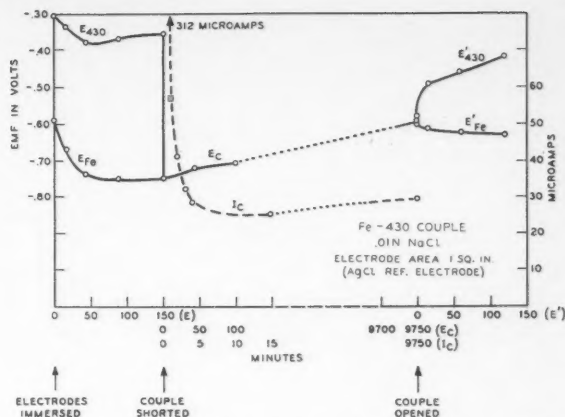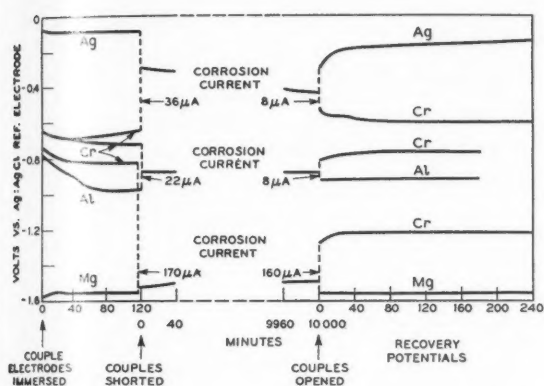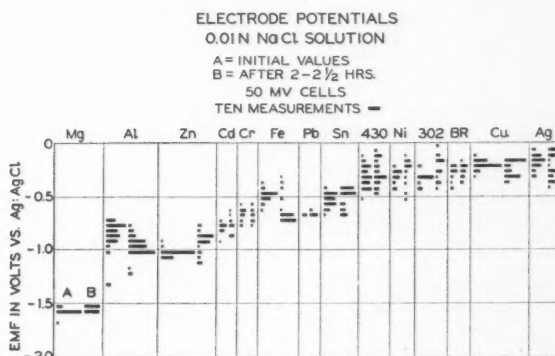e potentials and currents of four zinc-aluminum couples are plotted against time. As will be observed from the plot of galvanic corrosion current, the aluminum started as an anode but after about a thousand minutes its position with respect to zinc were reversed. Another example is shown in Figure 4 where iron is coupled to the chromium-iron alloy, type 430 steel.

Effect of Anode and Cathode Products

Of considerable significance is the effect of the products produced at the anodes and cathodes upon the potentials. In general the anodic metal is not affected as much as the metal acting as cathode. For example, chromium or a chromium steel will not be greatly affected when slightly anodic or cathodic to another metal, but when coupled to a metal like magnesium the large corrosion current will produce a highly alkaline and highly reducing condition in

the cathode film. The potential of chromium will be nearly a half volt more negative during the "recovery" period as illustrated by Figure 5.

Since the open circuit single electrode potentials vary over such a wide range, tables giving such values may be relatively meaningless. A series of histograms showing the values and spread at intervals of elapsed time aids in depicting the relative behavior of different electrodes. The data from a large number of measurements of single electrode potentials are shown in Figure 6. The values are shown for both the initial measurements and for a measurement made after the electrodes had been in contact with the electrolyte from two to two and a half hours. The length of the bars represents the number of measurements having a value within a 50 millivolt bracket or cell. In other words, all values between 1.00 and 1.05 volts are plotted at 1.025. In many cases it would be difficult to predict which metal would be anodic to another thus emphasizing the inadequacy of static single electrode potential measurements for predicting galvanic couple corrosion in any quantitative way.

Other Graphical Data

While measurements of the galvanic corrosion currents show some spread and change with time,
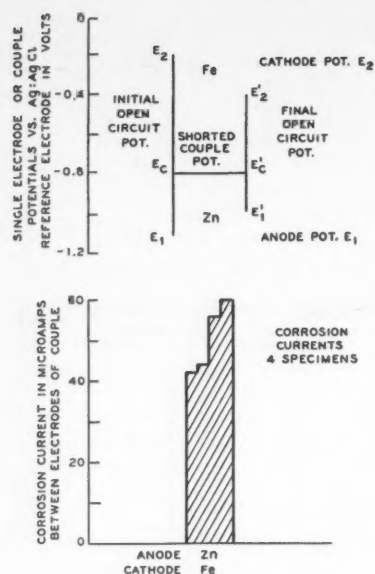
Figure 7—Explanatory chart for potential-current charts.

Figure 8—Corrosion currents and potentials of magnesium coupled to various metals in .01N NaCl.

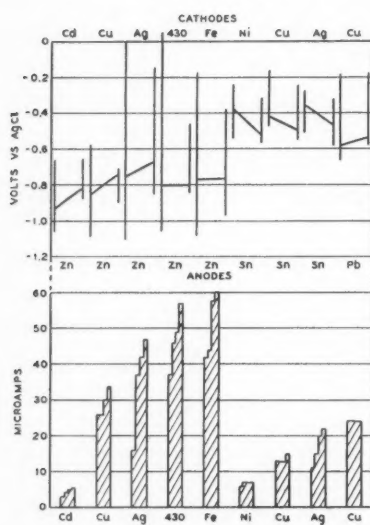Figure 9—Corrosion currents and potentials of aluminum coupled with various metals in .01N NaCl.

Figure 10—Corrosion currents and potentials of various couple combinations in .01 NaCl.

the direction and magnitude of the currents clearly establish which electrode is to be galvanically corroded and relatively how rapidly. If reversals occur it is usually under conditions where the currents are very small such as illustrated by Figure 3.

The currents of a representative group of quadruplicate samples have been averaged over a period of 100 to 1000 minutes and plotted with the maximum spread in averages of the potentials. These data are given in Figures 7 to 12, inclusive. As illustrated in Figure 7, the maximum potential difference of the open circuited couple is shown, with the potential

Figure 11—Corrosion currents of various couple combinations in distilled water.

Figure 12—Corrosion currents and potentials of various metallic couple-electrolyte combinations.

of the short circuited couple at both the beginning and end of the period, and the "recovery" potentials. The bar graphs show the average current for each one of the samples. The value of the potential of the short-circuited couple indicates the kind of polarization control; cathodic control being indicated by more negative values. For example, there is predominant cathodic control in the Mg-Fe couples, mixed

Figure 13—Corrosion currents at different time intervals of various couple combinations where magnesium, zinc and aluminum are anodes.

Figure 14—Corrosion currents at different time intervals of various couple combinations.

TABLE 2—Corrosion Currents for Various Metals

Approximate values of current which would cause the removal of 0.001-inch of metal by corrosion in one year from the specimens in these tests, which have a nominal area of 1 square inch.

Metal	Current (Microamperes)
Aluminum	13
Cadmium	7½
Chromium	20
Copper	7
Iron	14
Lead	5
Magnesium	14½
Nickel	14½
Tin	6
Zinc	10½

control in the Al-Ag couples in chloride solutions and anodic control in Zn-Al in neutral sulfate solutions.

In Figures 13 and 14 the average initial, fifteen minute and final currents are shown for all the couples which were studied in dilute sodium chloride solution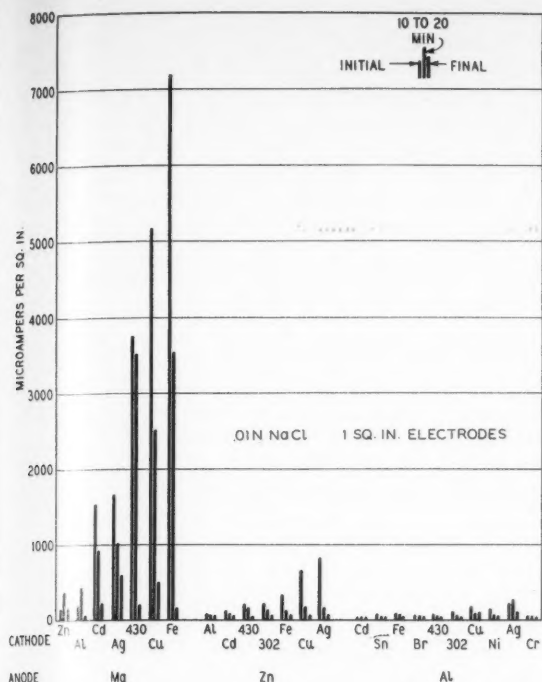. Particular attention should be paid to the magnitude of the current designated as final, which was usually taken after a short circuit period of eight to ten thousand minutes (six days). This current is indicative of what might be expected in service over a long time period.

Table 2 gives the approximate values of current which would cause the removal of 0.001 inch of metal by corrosion in one year from one square inch of surface. Consideration of the data in Figures 8 and 9 reveals that in the case of the Al-Cu couple exposed to a chloride solution under the conditions of this test, the loss would be 0.007 inch per year if the corrosion were uniform. On the same basis, the loss of the Mg-Cu couple would be around 0.034 inch. This is assuming that the average current shown would extend over a period of a year.

Couple Potential Differences

An examination of the data reveals that the couple potential difference, except in a very broad sense, is an unreliable guide as to the magnitude of the galvanic corrosion as realistically indicated by the corrosion current. For example, the potential between 430 steel and magnesium is not significantly different from that between copper and magnesium; yet the corrosion current of the former is only two-fifths that of the latter.

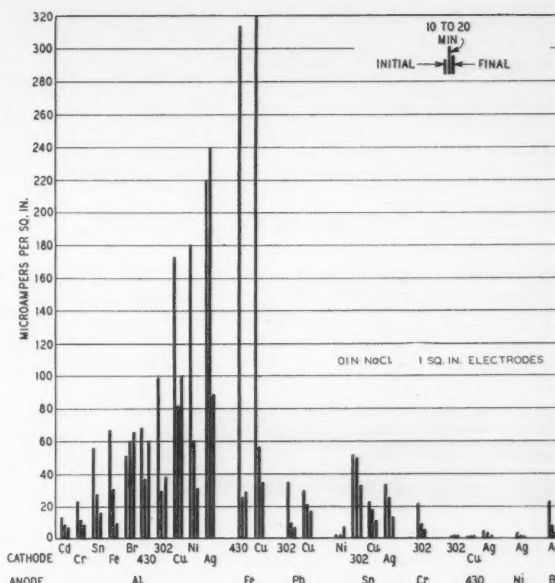About the same situation holds true for a comparison of nickel-aluminum and copper-aluminum. The

extreme reactivity of magnesium as a couple member is brought out by the data. For example, when coupled with copper, silver, or iron the corrosion current is more than six times as great as that of similar couples with aluminum. Its behavior in the presence of condensation is clearly indicated by the data in Figure 11. With distilled water saturating the filter paper separator, the current of a magnesium-430 steel couple is sixteen times that of an aluminum-430 steel couple. This is due for the most part to the high solubility and ionization of magnesium hydroxide and carbonate so that magnesium can be said to provide its own electrolyte.

Weight Loss Studies of Couples Exposed to the Atmosphere

The determination of rates of galvanic couple corrosion in the atmosphere is a much more complicated problem than most other corrosion measurements. The action is usually restricted to the immediate vicinity of the couple junction, hence weight losses or reduction of tensile strength may not be significant. The American Society for Testing Materials has long employed an assembly of washers bolted together as test specimens and has reported its results on several occasions.[2] In these specimens the action is confined to the edges of the washers and
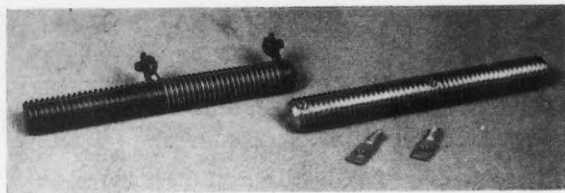
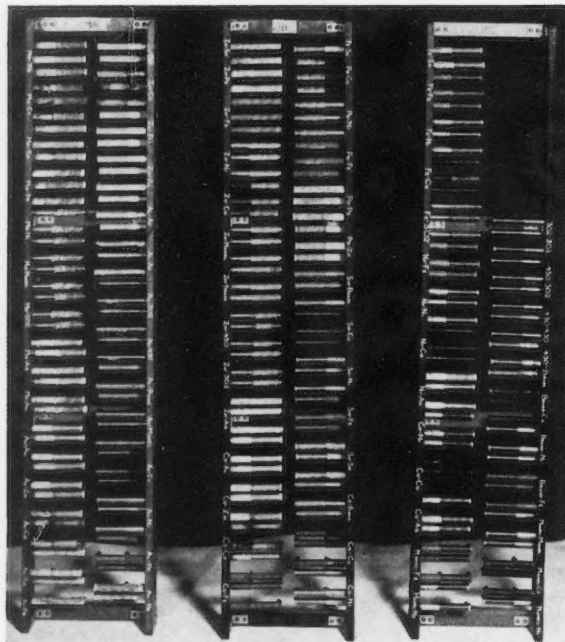Figure 15—Bolt and wire type galvanic couples.

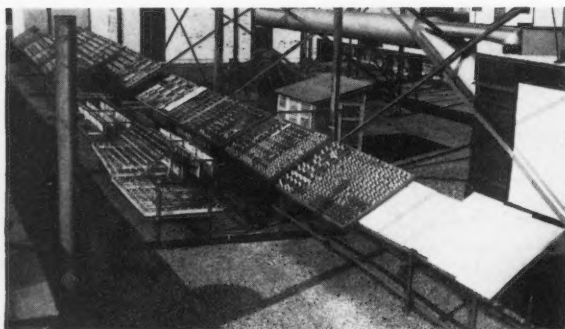Figure 16—Racks containing exposed bolt and wire type couples.

Figure 17—Roof exposure site in New York showing racks and louvered shelter.

weight loss measurements are not very sensitive. Furthermore, there is a tendency for these washer type couples to open circuit or develop a high resistance between elements.

A new type of couple has been developed* which does not have some of the shortcomings of the washer type. It is comprised of a threaded rod of the cathodic material on which is wound a wire of the anode material as shown in Figure 15. The surface

* This couple was developed originally at the Bell Telephone Laboratories by Mr. C. H. Sample who is now with the International Nickel Company.

at which corrosion can occur is large compared to the volume of the test specimen. Hence the test specimen will experience large changes in percent weight loss for relatively small amounts of corrosion. The wires and bolts are cleaned with solvent and handled with clean gloves so that no electrolytic contamination occurs. The wire is weighed, then wound on the bolt and the ends attached to the lugs to insure electrical contact. The ends of the wire and the lugs are covered with a bituminous coating to prevent corrosion at this point which might introduce a high resistance between the wire and bolt or cause an open circuit.

It has been found convenient to mount these couples in racks as shown in Figure 16. These racks are placed in a flat horizontal position when exposed. The terminal lugs are placed underneath the specimen in such a way that moisture will drip away from the specimen at that point. After exposure, the ends of the wire which are attached to the lugs and were coated with bitumen are clipped off, cleaned in boiling toluol and weighed. The weight of these ends is subtracted from the initial weight of the whole wire to give the weight of the specimen actually exposed as a couple in intimate contact with the bolt.

In this study the corrosion products were removed from wire specimens of brass, copper, monel, iron, lead, tin, nickel and corrosion resisting steel by electrolyzing as the cathode in a bath containing 5 percent H_2SO_4 and 0.2 percent "Rodine" inhibitor. Cadmium specimens were cleaned by immersion for 2½ minutes in a 10 percent solution of NH_4Cl, held at 70 C. Zinc wires were given the same treatment, but in addition had a 15 to 20 second immersion in a boiling solution containing 5 percent chromic acid and 1 percent silver nitrate. Aluminum received a 5 minute treatment, with brushing, in a solution containing 30 grams of chromic acid and 25 cc of 85 percent phosphoric acid per liter. Magnesium wires were cleaned for 30 seconds in a 20 percent solution of chromic acid containing 1 percent of silver nitrate. These cleaning procedures were applied to clean uncorroded wires to determine the losses in weight due to cleaning so that a correction factor could be applied to the weight of the corroded specimens after removal of corrosion products.

Three representative exposure sites were selected, Point Reyes, California, a roof in New York and a tropical jungle location in Panama. The test site at Point Reyes is located on the windswept Pacific beach about thirty-five miles north of San Francisco, and is characterized by westerly winds from the ocean, frequent fogs and nightly dews, with little rain to wash away the accumulation of sea salt. The New York roof site was that formerly used by the ASTM for corrosion exposure of nonferrous metals and electroplated coatings, and is characterized by contamination from flue gases and the fumes from industrial plants. The Panama test site was in the jungle behind Fort Sherman on the Atlantic side of the Canal Zone, and is representative of a severe tropical exposure.

In all three locations some of the specimens were boldly exposed to the weather and others were placed
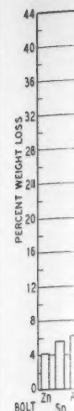
Figure 18—Bolt and wire couples (percent weight loss of magnesium wire per 100 days of bold exposure).

in a louvered shelter which was essentially a Stevenson screen, a box used for housing meteorological instruments, which allows free circulation of external air. This shelter is shown as installed on the New York roof in Figure 17.

In addition a group of specimens was placed in a cycling humidity room which was designed to simulate a severe but sheltered tropical environment such as might be en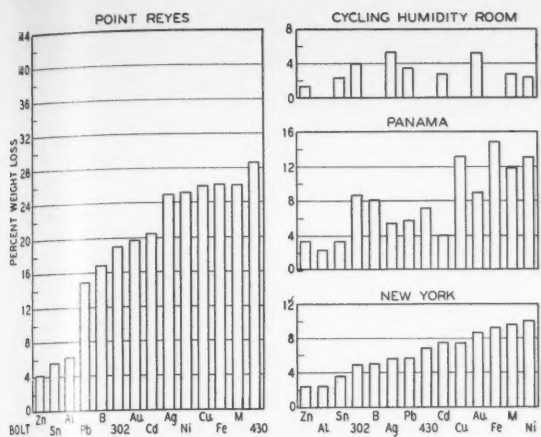countered during shipment or storage of metallic material. The cycle consists of a steady period of 3 hours at 80 F, a rise over a period of one hour and a half to 120 F where the temperature is held for four and a half hours, then a drop back to 80 F over a three hour period; all at a nominal relative humidity of 95 percent.

Each combination of metals was exposed in triplicate. A set of blanks comprised of bolts and wires of the same metal were exposed along with the couples to determine the rate of corrosion in the various environments of specimens that were not coupled to a dissimilar metal. This rate was subtracted from the observed combined rate of corrosion to give that due to galvanic couple action alone, assuming the effect of the superimposed galvanic corrosion upon the simple atmospheric corrosion to be negligible.

At Point Reyes and New York two sets of specimens were given the bold exposure. One set was exposed for approximately 90 days and the other set together with the specimens in the shelter were exposed for about 150 days. The Panama and cycling humidity room specimens were all exposed for the 90 day period. The data are given in Figures 18 to 23, inclusive. In addition the data for a few representative couples have been plotted in Figure 24 to show the correction for the blank in the case of both exposed and sheltered specimens.

The data for many of the samples containing magnesium wire may be in error on the low side, as many wires broke due to stress corrosion cracking and lost intimate contact with the bolt. This breakage appeared to be unavoidable in severely corrosive environments with this particular magnesium alloy (FS-1). Various efforts to minimize stress and avoid
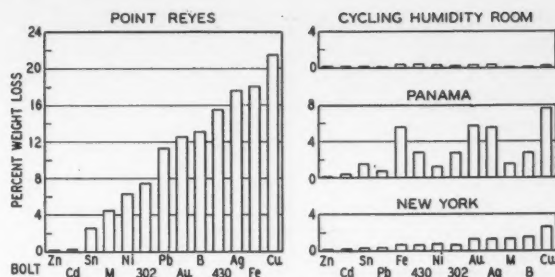

Figure 19—Bolt and wire couples (percent weight loss of aluminum wire per 100 days of bold exposure).
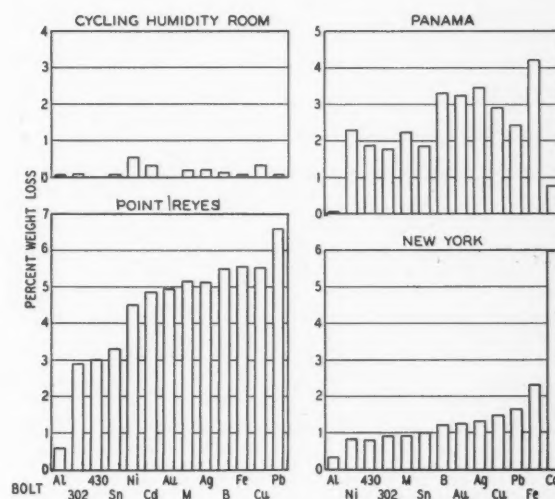
Figure 20—Bolt and wire couples (percent weight loss of zinc wire per 100 days of bold exposure).
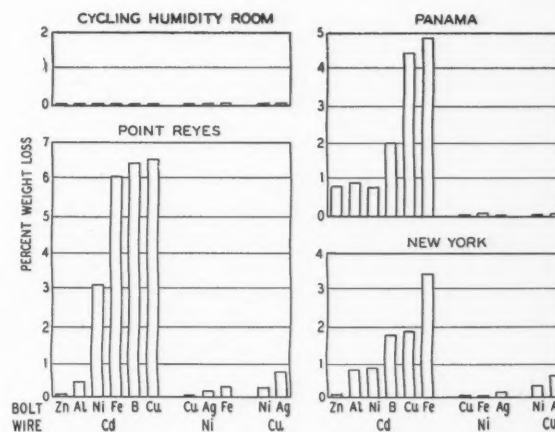
Figure 21—Bolt and wire couples (percent weight loss of wires per 100 days of bold exposure).

breakage were without success. No breakage occurred in the case of the other wires.

An inspection of the data will confirm earlier statements that the relative corrosion is not related to tables of potentials except in a general way. The metals can be divided into rough groups based on their galvanic corrosion tendencies as a whole. Con-

Figure 22—Bolt and wire couples (a second graph showing percent weight loss of wires per 100 days of bold exposure).

Figure 24—Effect of shelter on weight loss of galvanic couples.

siderable individual variation will be noticed from one environment to another.

It will be noted that several apparent anomalies appear in the data on percentage weight loss. In Figure 19 zinc is shown as causing a slight galvanic corrosion of aluminum whereas in Figure 20 aluminum is shown as causing the galvanic corrosion of zinc. This same situation was revealed in the corrosion current measurements. A similar relationship exists with respect to nickel and copper.

In some cases, iron tends to promote galvanic corrosion of metals normally presumed to be more noble. This may be due to the "passive" state of iron under the conditions of the test or to the presence of an oxide coating on the iron which makes it more cathodic. It is well known that oxide on iron such as mill scale is cathodic to active iron. In practically all cases, iron appears to cause more galvanic corrosion than its potential in the active state would indicate.

Figure 23—Bolt and wire couples (percent weight loss of wires per 100 days of sheltered exposure.)

Discussion

In any discussion of atmospheric corrosion, one is confronted with definitions of exposure conditions which range from very severe exposures in a marine or industrial atmosphere to the mildness of a dry indoor environment. The exposure under two conditions, boldly "exposed" and "sheltered," at the sites described in this paper form a good basis for comparisons. Interpolation or extrapolation to other conditions can be made by reference to the relative corrosion experienced by representative groups of uncoupled metals. The weight loss data indicate that the marine atmosphere at Point Reyes is considerably more severe from the point of view of galvanic corrosion, than either that of New York or Panama. The last two are somewhat comparable, with differences due largely to the behavior of individual couples.

The bolt and wire type of couple has proven to be an excellent means of quickly assessing the relative behavior of different combinations of metals by the weight loss method. Where stress corrosion cracking occurs, this method may not be reliable if the wire loses intimate contact with the bolt. But in most cases, even if the wire breaks, the electrical contact is maintained and the wire remains close enough to the bolt to insure continued galvanic corrosion.

Measurements of the galvanic couple corrosion currents as described in this paper provide a quick means of determining the probable relative corrosion behavior of couples. The method is more realistic than merely measuring potentials at some arbitrary time in that it shows the effect of polarization and surface protective films in controlling the rate of corrosion. In the case of magnesium it reveals the effect of the alkaline reaction products of the metal when in contact with condensation. Among its limitations is the partial exclusion of air from the corroding surfaces which might produce some distortion in the relative rates of corrosion of various combinations of metals.

The agreement between weight loss data and the relative magnitude of the final corrosion currents is good except in a few cases. The large corrosion cur-

rents of the Mg-Cu and Mg-Ag couples would indicate a larger relative weight loss than was obtained in these experiments. This may be explained as resulting from the breaking of the magnesium wires after a short period of exposure and the loss of an intimate contact between anode and cathode. A reverse situation exists in the case of Al-Fe and Zn-Cd couples where the weight loss data indicate a higher relative rate of corrosion than the comparable data on corrosion currents.

From a study of the data a galvanic series can be prepared, but only as groups (see Table 3). Members of the series will usually suffer galvanic corrosion when coupled to a member of a group below it in the series. However, conditions may be such that a reversal occurs. For instance, under some conditions, zinc will be galvanically corroded by aluminum and copper by nickel or nickel-chrome steels. Where these reversals occur, the magnitude of the effect is generally rather small. The magnitude of the corrosion produced will depend upon how far apart the metals are in the series, the polarization characteristics of the couple and other factors of environment and exposure.

Normally the metals within each group can be considered as compatible with each other, but under certain circumstances galvanic couple corrosion can occur within the group. For example, copper-rich aluminum alloys in contact with pure aluminum will produce galvanic corrosion on the latter if wet with sea water. Lead and tin coatings on steel are a familiar example of the galvanic corrosion of steel at pores. Here the large ratio of cathode surface to anode surface prevents the normal cathodic control of polarization and the galvanic current, even though the potential differences are small. Another example may be found in the corrosion resisting steel alloy family where, under some conditions, 430 type steel will be badly corroded by contact with type 316.

From the information in Figures 13 to 22 and elsewhere in this paper it is apparent that magnesium alloys cannot be "exposed" to the weather in a severely corrosive atmosphere when coupled with most other metals. Only aluminum, zinc and tin appear to have a small enough effect that it seems reasonable to expect organic coatings to protect couples of magnesium and these metals. With the large potential differences and galvanic corrosion currents between magnesium and other metals it is unrealistic to expect organic coatings to protect a couple when exposed to a marine atmosphere. The sea salt solution can be expected to bridge the couple in some manner (either through holidays, cracks or pores or by simple permeability as the organic coating ages) and to permit a galvanic current to be initiated. This current will produce alkaline products that will tend to cause blistering and peeling of the organic coating with subsequent loss of protection. On the other hand, the great decrease in galvanic corrosion which accompanies a "sheltered" exposure of magnesium couples permits their use when they are suitably finished with an organic protective coating.

Aluminum and its alloys are in somewhat the same category as magnesium with regard to exposure as couples. However, since the potentials and galvanic corrosion currents are lower and aluminum may be given a protective oxide coating by anodizing, adequate protection can be provided. Bare aluminum coupled to a more noble metal will give severe corrosion trouble in an "exposed" marine environment. When anodized and painted it will be satisfactory unless the coatings are damaged at or near the couple junction. In addition to the more favorable potential and galvanic current situation, the products produced by the current are less destructive to the protective coating. In a "sheltered" exposure, bare aluminum will not suffer severe corrosion unless coupled to one of the metals in Group V. "Indoors," it will be essentially free from all dangers of significant galvanic couple corrosion.

Zinc and cadmium, which for the most part will appear as protective coatings on steel, will suffer in much the same manner as aluminum, unless phosphatized and painted when "exposed." When "sheltered" or "indoors," their performance will be much the same as aluminum. (Note: Bare zinc and cadmium will develop white corrosion products under conditions of high humidity and condensation unless provided with a protective coating.)

The metals in Group III and IV will be subject to galvanic corrosion when coupled to a member of a more noble group and "exposed" to the weather but at a much lower rate than in the case of Groups I and II. When "sheltered" or "indoors," no significant galvanic couple corrosion is to be expected.

The studies described in this paper do not take into account the measures sometimes employed for the mitigation of galvanic corrosion. The use of insulating washers, elaborate organic protective coatings or the interposing of more compatible materials between the principal members of the couple (such as aluminum between magnesium and stainless steel) may be helpful in some cases. These measures become less reliable as the conditions become more severe and the combination of metals forming the couple becomes more active. Adequate tests have not been developed which give data which are useful in predicting the behavior of "protected" couples short of actually constructing models and exposing them, particularly since factors such as physical abuse, weathering, and required service life introduce variables in addition to those normal to atmospheric exposure.

Acknowledgment

TABLE 3—Galvanic Series Prepared From a Study of Test Data

I	II	III	IV	V
Magnesium	Aluminum, Zinc, Cadmium	Iron and Carbon Steels, Lead, Tin	Nickel, Chromium, Corrosion Resisting Steels (Types 430, 302, 316, etc.)	Copper-Nickel and Copper-Zinc Alloys, Copper, Silver, Gold

Laboratories, Fort Monmouth, N. J., for the conception of the project and the inspiration given to it.

References

1. H. H. Uhlig. Corrosion Handbook, John Wiley and Sons, 1948. Pages 415-426, 481-496.
2. Reports of Subcommittee VIII on Galvanic and Electrolytic Corrosion ASTM B-3. *Proceedings, ASTM,* **35,** 167 (1935); **39,** 247 (1939); **48,** 167 (1948).
3. H. P. Godard. Galvanic Corrosion. *Chemistry in Canada,* **2,** 51 (1950).
   M. R. Whitmore and J. Teres. Dissimilar Metal Couples—Corrosion Resistance from Current and Potential Measurements. *Ind. Eng. Chem.,* **31,** 608 (1939).
   U. R. Evans. The Practical Problems of Corrosion. Part V. Corrosion and Protection at the Contacts of Dissimilar Metals. *Trans., Soc. Chem. Ind.,* **47,** 73T (1928).

A. B. Lauderbaugh. The Fundamentals of Galvanic Corrosion. *Gas Age,* **106,** No. 5, 20 (1950).
R. H. Brown. Galvanic Corrosion. *Bulletin, ASTM,* **126,** 21 (1944).
W. A. Wesley. Controlling Factors in Galvanic Corrosion. *Proceedings, ASTM,* **40,** 690 (1940).
F. L. LaQue and W. D. Mogerman. Notes on Galvanic Corrosion. *World Oil,* **129,** 153 (1949).
M. E. Parker. Bimetallic Corrosion. *Oil and Gas J.,* **50,** No. 13, 81 (1951).
H. D. Holler. Some Electrical Relations in Galvanic Couples. *J. Res. Natl. Bur. Stan.,* **45,** No. 5, 373 (1950).
G. T. Colegate. Galvanic Corrosion and Its Practical Significance. *Metal Treatment,* **15,** No. 56, 183 (1948).
S. B. Ashkinazy and J. M. Joyce. Galvanic Corrosion—What It Is and How It Can Be Avoided. *Materials and Methods (U.S.A.),* **31,** No. 2, 49 (1950).
H. Silman and A. Freeman. Contact Corrosion in Metals. *Sheet Metal Industries,* **15,** 1129 (1941).

Any discussions of this article not published above will appear in the December, 1955 Issue.

---

ol. 11

orro-
6, 21
sion.
Cor-
No.
ples.
Sig-
What
hods
etals.

Figure 2—View of wing tank corrosion. Note accumulation of scale and rust deposits.

Countermeasures for Control
Of Internal Corrosion Of a Tanker Ship*

By CHARLES P. DILLON

Introduction

THIS ARTICLE reviews laboratory and field corrosion data derived in connection with the internal corrosion problem of the S.S. R. E. Wilson, a T-2 tanker owned by Carbide and Carbon Chemicals Company, a division of Union Carbide and Carbon Corporation and operated by the Marine Transport Company of New York, New York.

The corrosion problem arises from cyclic exposure of the internal compartments to sea-water, marine atmospheres and hydrocarbon cargos during the transportation of chemicals and hydrocarbons between the Texas Gulf Coast and the eastern seaboard. Applicability of accepted counter-measures to the R. E. Wilson's specific mode of operation was undefined at the time the problem of internal corrosion was recognized and it was necessary to establish the mechanisms of corrosion, the influence of operating variables and the effectiveness of individual remedial measures for the operating conditions.

Anticipated direct costs of internal corrosion for the S.S. R. E. Wilson during the period 1955 to 1967 are estimated to be $125,000 annually. This figure derives from the estimated costs of $1,850,000 for replacements during this 12 year period, of which some $375,000 is unavoidable, regardless of counter-corrosion measures, because of the present condition of the vessel.

It is highly desirable to extend the life of the ship, if possible, by counter-corrosion measures rather than make expensive repairs necessary if the vessel is to continue in use for the next ten or twelve years.

The Ship—A tanker ship is essentially a floating, compartmented storage tank. The S.S. R. E. Wilson is a T-2 tanker of approximately 5,000,000 gallons capacity. The vessel is 524 feet in length, 68 feet

CHARLES P. DILLON—Corrosion Engineer for Carbide and Carbon Chemicals Co., Texas City. A 1942 graduate of Georgetown University in Washington, D. C., he holds a BS in chemistry. With the exception of four years as an air force meteorologist he has been with Carbide since graduation. Actively engaged in corrosion and metallurgical work since 1948, his principal fields of interest are organic chemical process corrosion, cooling water corrosion and tanker problems.

Abstract

Internal corrosion in wing tanks of a tanker ship, the SS R. E. Wilson is estimated to cost $125,000 annually. Corrosion mechanisms are described in terms peculiar to the operation of this ship. Various counter measures are considered, including coatings, inhibition of cargo and ballast, use of inhibited fresh and sea water, changes in Butterworthing schedule, cathodic protection with and without concurrent inhibition. Both laboratory and in-service tests are reported for numerous mitigation methods. It has been established tentatively that the best solution for this ship is concurrent inhibition of cargo with an oil-soluble inhibitor and treatment of empty tanks with a soluble-oil inhibited salt water wash. Reduction of corrosion up to 75 percent is expected with a net annual saving on the order of $65,000.
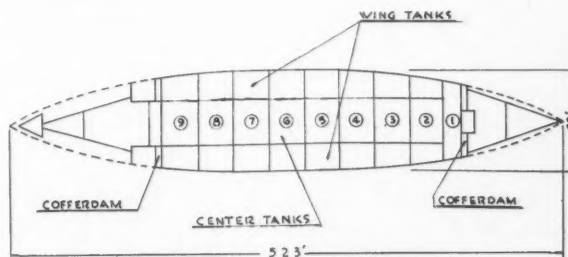
Figure 1—Diagram of tank arrangement.

across the beam, with a dead weight carrying capacity of 16,190 tons.

Distribution of the cargo compartments is illustrated in Figure 1. The eighteen wing tanks have a capacity of about 2½ million gallons, while an equal volume can be carried in the nine center compartments. The cargo tanks are separated from the fuel bunkers and dry cargo holds by void spaces known as cofferdams. The appearance and arrangement of similar ships have been described in detail in the literature.[1, 2, 3, 4]

Operation—The S.S. R. E. Wilson carries refined synthetic organic chemicals in the center compartments, while the wing tanks are leased for the transportation of refined hydrocarbon cargos. The cargo is transported from Texas City, Texas, to the terminal at Carteret, New Jersey, during a voyage of 5 to 6 days duration. On the return trip, sea water ballast is carried in approximately half of the wing tanks to trim the ship, the remainder of the tanks being empty.

While there is no significant corrosion of the chemical compartments of the vessel, the wing tanks undergo moderate to severe corrosion as may be seen in Figure 2, depending upon operating variables.

The Fish, Game and Oyster Commission of the State of Texas requires ballast discharged at the Texas City docks to be non-toxic to marine life. The criterion is applied to the undiluted ballast, because it is assumed that only diffusion processes will govern its dilution in the slip.

Ballast loaded in a tank recently discharged of hydrocarbons is inevitably highly toxic to marine life by virtue of contamination with residual cargo. This is known in the trade as "dirty" ballast. When tanks are cleaned with the commercial high-pressure, high-temperature sea water wash known as "Butterworthing" or "Pyrating," subsequently loaded ballast will be non-toxic or "clean."

To so prepare the wing tanks prior to embarkation on the ballast leg of the voyage would be expensive, because of the delay in the use of the ship. It is therefore necessary to load "dirty" ballast and depart on the southerly voyage. The other wing tanks are Butterworthed and take on clean ballast en route, the dirty ballast being discharged to the open sea. In this manner, the vessel arrives at Texas City with a non-toxic ballast which can be discharged at will, either in the bay or in the slip, as weather demands.

The ballast duty is rotated between odd- and even-numbered tanks. As will be shown later, this mode of operation is superior—under the conditions of operation of the R. E. Wilson—to the "fixed" ballast pattern sometimes employed by other operators. The latter type of operation restricts certain tanks from ballast, while other tanks in some geometrical pattern, e.g. athwart-ships, carry ballast each trip.

Normal operations of the S.S. R. E. Wilson have been such that after discharge of cargo and loading of dirty ballast, the other tanks were Butterworthed immediately and filled with clean ballast. After discharge of dirty ballast, the empty tanks during the remainder of the southerly voyage are water-wet and exposed to marine atmosphere, a severely corrosive condition.

One proposed method of operation entailed making the entire ballast voyage with dirty ballast—leaving the empty tanks "cargo-wet" — and effecting the change to clean ballast at the Texas end of the ballast leg. The proposal was intended to minimize corrosion in empty tanks, but is of doubtful practicality because of the uncertainties of operation occasioned by weather, mechanical difficulties, etc. Any delay in ship operation is, of course, extremely costly.

A second suggested mode of operation would entail carrying ballast in all wing tanks each return trip. While this would eliminate atmospheric corrosion, the financial losses from increased time enroute and increased fuel consumption easily could offset the potential saving resulting from the reduction in corrosion.

At present, it is believed that the normal operation, plus certain remedial measures, is preferable.

Corrosion Mechanisms—The general mechanism of attack is the corrosion of steel by sea water at the metal surface in the presence of oxygen. Both water and oxygen are necessary in order for the corrosion to proceed. The mechanisms have been described previously.[5]

In a ballasted tank, the sea water functions not only as the electrolyte but as a reservoir of dissolved oxygen. The corrosion rate is not normally excessive.[2, 3, 4, 6, 7]

Corrosion is greater in a cargo-loaded tank, because the metal is wet with sea water from previous exposures and because the solubility of oxygen is six to eight times greater in the light hydrocarbons than in sea water. There appear to be only minor differences in the corrosivity of the light hydrocarbons carried, e.g., gasoline, kerosene and heating oil.

The conditions for atmospheric corrosion in an empty tank are somewhat more complex.

Corrosion is very severe in an empty tank which has been wetted with water immediately prior to atmospheric exposure. In this case, there is ample electrolyte and a supply of oxygen unlimited by solubility or diffusion considerations.

Experience on the S.S. R. E. Wilson and in laboratory tests simulating the corrosive conditions, has been that corrosion of empty tanks is light when the metal has not been water-wet between the cargo and atmospheric exposures. This is true particularly in the center compartments, whose cycle of exposure is refined aliphatic chemicals and marine atmosphere only. Figure 3 shows the light even rusting and absence of scaling or marked wastage in a center tank. The low rate in cargo-wet tanks has not been reported previously except as isolated exceptions to the generalization about severe corrosion in empty tanks. This lower rate may be due to one or more of several mechanisms. First, the water present on the metal during the cargo leg may have been nearly all consumed by corrosion. Second, there is a definite, although limited, solubility of water in hydrocarbons (on the order of 8-10 gallons per wing tank of gasoline) and this may aid in dessicating the scale on

the metal surface. Third, a residual film of hydrocarbons on the tank wall (or coupons) may constitute an effective barrier against atmospheric attack.

Regardless of the governing mechanism, a distinct diminution of corrosion of these tanks as compared to tanks with water-wet atmospheric exposure has been observed on specimens in both laboratory and field tests.

Condensation on walls of empty tanks might cause serious corrosion in the atmosphere even when there is no other wetting between the cargo and atmospheric exposures. Whether or not this is a significant source of attack in practice is a moot point. The likelihood of condensation is governed by water temperature in the adjacent (ballasted) tank, efficiency of heat transfer through the scaled bulkheads, ambient temperature in the empty tank and the absolute and relative humidities of the air in the empty tank. It should not be *assumed* that such condensation will occur in every case or in most cases. Further investigation is required.

Representative average corrosion rates of each of the phases discussed—with the exception of the condensation phenomenon—are given in Table 1. These data are taken from years of service as well as laboratory and field corrosion tests, with the exception of the figure for atmospheric corrosion in the absence of wetting. This exception is an interpolation from laboratory and field tests on the S.S. R. E. Wilson and from representative data in the literature on corrosion rates for moderate to severe atmospheric exposures.[6] These corrosion rates will vary due to diurnal or seasonal temperature changes, but probably will stand in approximately the same ratio of severity regardless of absolute rate under any given set of conditions.

An estimate of corrosion to be expected under conditions of cyclic exposure may be made from a consideration of the duration and intensity of each phase of the cycle. Table 2 illustrates this approach for a rotating ballast pattern in which each tank is exposed to cargo one half of the time and one quarter of the time each to ballast and to wet atmospheric corrosion. Relative severity of the three phases stands in the ratio 4:3:2 for the wet atmospheric, cargo and ballast exposures respectively.

Some deviation of the calculated average will occur in practice due to changes in the nature of the corrosion products on the metal surface. For instance, the chemical and physical condition of rust or scale accumulated in long-term exposure to any one phase will not necessarily be the same as that which results from cyclic exposure of the same duration. However, the calculated rates check well with average rates observed in service. Further, calculating back from average field corrosion rates and breaking them down according to the duration of exposure to each phase of the cycle, the calculated severity rates for each phase check well with experimental data. Table 3 illustrates the calculated and observed corrosion rates for several types of cyclic exposures.

Effect of the Butterworthing operation upon the corrosion rates should not be overlooked, but it is believed that sometimes it has been over-emphasized.
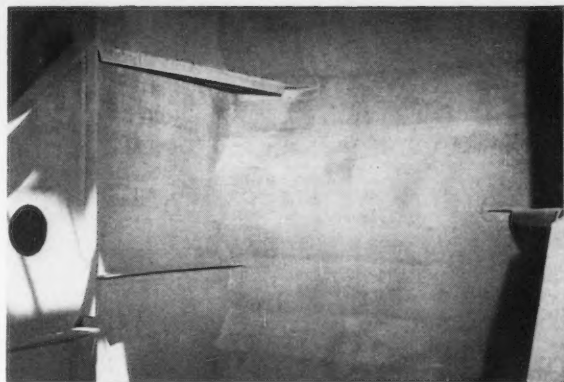
Figure 3—Internals of center tank used for carrying refined aliphatic organic chemicals with alternate exposure to marine atmosphere. Note absence of pitting and scaling.

TABLE 1
Representative Corrosion Rates for Individual Phases of Exposure

Phase	Penetration IPY
Wet marine atmosphere	.010
Gasoline on pre-wetted surface	.008
Seawater	.005
Atmospheric exposure	.004

TABLE 2
Calculation of Anticipated Corrosion for a 4-Way Cycle (Rotating Ballast Plan)

Exposure	Rate, IPY	Duration Percent	Penetration, IPY
Wet atmosphere	.010	25	.0025
Gasoline	.008	50	.0040
Ballast	.005	25	.0013
		Resultant Average Rate	.0078

TABLE 3
Comparison of Calculated vs. Observed Rates of Corrosion Under Different Cycles of Exposure

PHASE	Severity	Duration Percent	Corrosion, IPY	Observed Rate (1000 Hr.)
A. Alternate Seawater-Gasoline Exposure				
Gasoline	.008 IPY	50	.0040	
Ballast	.005	50	.0025	
Average	....	..	.0065	.006–.008
B. Alternate Gasoline-Wet Atmospheric Exposure				
Gasoline	.008	50	.0040	
Wet Atmospheric	.010	50	.0050	
Average	....	..	.0090	.008
C. Alternate Gasoline-Atmospheric* Exposure				
Gasoline	.008	50	.0040	
Atmosphere	.004	50	.0020	
Average	....	..	.0060	.004

* Specimens not water-wet between hydrocarbon and atmospheric exposure.

If a tank is not normally wetted between the exposures to cargo and to atmospheric conditions, for instance, severe corrosion will be caused by a Butterworthing operation between the two exposures. This is due to the fact that the metal surface is wetted with sea water immediately prior to exposure to air. If, on the other hand, a tank is water-wet anyway, as from having been discharged of ballast, an additional Butterworthing should have very little effect.

It should be noted, however, that the impingement
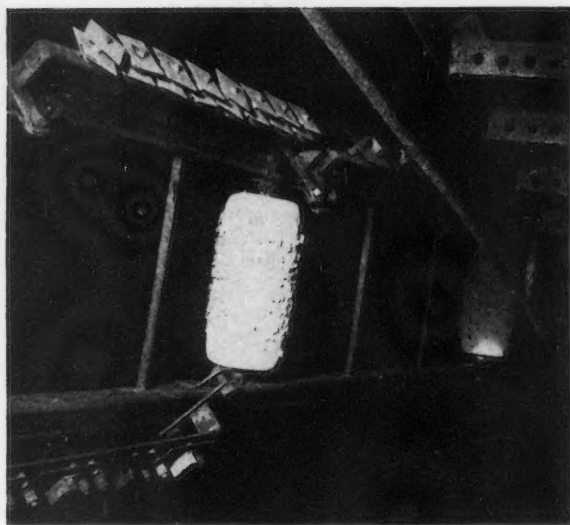
Figure 4—Anode field corrosion test rack installed on anode ladder. Outer row of specimens grounded to anode system, inner row insulated for comparison.

TABLE 4
Laboratory Tests on Effect of Butterworthing Temperature, Alternate Gasoline: Seawater Exposure

Condition	336 Hours	672 Hours	1006 Hours	2012 Hours
Hot Butterworth.....	.009	.007	.007	.008
Cold Butterworth....	.007	.008	.006	....

of the high-pressure wash may accelerate *localized* corrosion by removal of rust and scale.

It has been suggested that the elevated temperature of the Butterworthing operation may contribute to faster corrosion. A procedure was developed, therefore, which entailed a cold sea water wash, using the Butterworthing nozzles and pumps, with successful cleaning and gas-freeing obtained by adding a sea water-soluble wetting agent, "Tergitol NPX" (a UCC Trademark). Field corrosion tests during this period, as well as corroborative laboratory tests, indicated that the temperature of the Butterworthing stream did not affect the corrosion rate (Table 4). This is not surprising when the brief exposure to the sea water wash is considered, although the Butterworthing sometimes has been considered to be a corrosive factor per se.

Corrosion Tests—Simultaneous laboratory and field corrosion tests were begun in an effort to study the variables involved in internal corrosion of the S.S. R. E. Wilson and the applicability of the several countermeasures.

Field corrosion tests were conducted on coupons and panels exposed in wing tanks of the vessel, operating conditions being restricted in certain tanks to determine effects of specific variables upon corrosion rates. Corrosion test racks were exposed in the bottom, middle and top sections of the tanks. Specimens were insulated electrically from the racks, except when the efficacy of an experimental anode installation was being studied. A typical corrosion

rack is shown in Figure 4. The specimens were prepared, cleaned and evaluated according to standard corrosion testing techniques.

During the course of the laboratory test program, a number of techniques and apparati were employed. All eventually devolved to a simple Erlenmeyer flask set-up containing a number of specimens, an aerator and the medium appropriate for the cycle of exposure. A humid marine atmosphere was supplied to all flasks by a stream of air which was sparged through a reservoir of sea water and delivered through a manifold to the individual flasks.

The Butterworthing operation was simulated originally by immersing the specimens in a sea water wash circulated by a laboratory pump. It later developed that the same results could be accomplished—corrosion-wise—by a simple washing procedure in a beaker, with the sea water agitated by air-sparging.

Special techniques used in studying individual phases (atmospheric corrosion and its inhibition, for instance) in every case ultimately gave way to long-term cyclic exposures in the Erlenmeyer flasks under conditions duplicating as closely as possible the cycle of exposures representative of the mode of operation being studied.

The outstanding feature of the laboratory tests was that complicated, but especially short-term, tests sometimes gave spectacular results in the evaluation of some particular treatment or factor. However, most of these results disappeared in long-term testing under cyclic conditions.

It was concluded that tests of from 1000 to 2000 hours' duration are required to establish data comparable to field test results. A typical testing cycle might be for instance

Atmospheric exposure ....One day
Ballast ....Six days
Cargo ....Seven days
Ballast ....One day
Butterworth ....30 minutes
Atmospheric exposure ....Six days
Cargo ....Seven days

This would correspond to exposure of a tank for four weeks with a rotating ballast pattern. When several specimens are exposed and one specimen is evaluated at the end of each cycle, reliable and reproducible results can be obtained.

Counter-Corrosion Measures—In general, counter-corrosion measures may be divided into two classes. The first consists of a number of techniques including changes in materials of construction, increased thickness of structural members and the use of coatings. The second consists of a group of treatments which have in common the principle of controlling the corrosive environment. In the second class, dehydration of one or more of the phases, removal of oxygen, use of fresh water, chemical inhibition of one or more of the phases and cathodic protection may be included.

These measures vary widely in their applicability depending upon the age of the ship and its operation as regards duration of each phase of the cycle. For instance, a cathodic protection installation is operative only when a conducting medium is present.

Another variation arises from the toxicity limitations on ballast. Certain operators may find that some

protection, especially if caused by substantial changes in the conditions at the metal surface or in the scale, may carry over from one exposure to another, particularly if undisturbed by cleaning operations. Toxicity requirements for the ballast on the S.S. R. E. Wilson, however, as previously described, entail frequent Butterworthing. This cleaning schedule strongly militates against carry-over of protection from one type of exposure to another.

Applicability of Counter-Corrosion Measures to the S.S. R. E. Wilson

Operation of the S.S. R. E. Wilson is based on a rotating ballast pattern. Two possible modes of operation in this pattern are: Changing to clean ballast immediately out of the northern port ("Normal Operation") or delaying the change until the last possible moment out of Texas City.

The rotating ballast pattern is justified because corrosion of empty tanks is severe under normal operating conditions. The rotating pattern equalizes corrosion between ballasted and empty tanks. Under delayed Butterworthing conditions, the corrosion rate in empty tanks is of the same order of magnitude as that of ballasted tanks, so a fixed pattern would offer no advantage and would be less versatile. A possible exception to this (e.g., where cathodic protection is employed) is considered in detail later. Table 5 illustrates corrosion rates in empty and in ballasted tanks under both methods.

Following is a detailed discussion of the applicability of individual counter-measures under the conditions prevailing in S.S. R. E. Wilson.

Materials of Construction—Substitution of alloyed materials for mild steel normally used in tankers is being considered by other investigators. The preponderance of data from other sources[7, 8, 9] indicates that low alloy steels are superior to mild steel for atmospheric exposure but little better in water-immersion service—with the possible exception of increased pitting resistance. It is possible that some advantage would be gained in cyclic exposures and this should be demonstrated finally in performance of certain experimental barges and alloy compartments in some of the new tanker hulls.

Such an approach is of doubtful merit for the S.S. R. E. Wilson, which has seen more than half of its expected service life and it is not under consideration for replacement of structural members.

Increased Scantlings—Increasing the thickness of structural members to offset corrosion normally is expensive compared to other remedial measures. It is obvious that this approach, like the first, is limited to new or replacement parts. It is not being considered because the primary object of the present investigations is to prolong the useful life of the vessel with a minimum of replacement and repair.

Coatings—Isolation of metal from its environment with a barrier film will eliminate corrosion effectively. The practicality of such a technique deserves thorough study.

	336 Hours	672 Hours	1008 Hours
A. Ballast Tanks			
No delay	.009	.007	.007
Delay	.007	.006	.006
B. Slack Tanks*			
No delay	.012	.009	.008
Delay	.005	.004	.003

* Gasoline inhibited.

Inorganic coatings are not considered economically feasible, the initial cost being estimated at a minimum of $1.50/sq. ft. for zinc metallizing, for instance. A zinc coating also has the further objection that it may have an adverse effect on certain hydrocarbon cargoes.[3] Coating with a metal more noble than the structural steel would be both uneconomical and dangerous from the standpoint of galvanic corrosion at holidays in the coating.

Organic coatings were viewed more favorably, on the basis of the work done by Cranmer,[10] who reported that vinylidene chloride-acrylonitrile or vinyl coatings might be effective solutions to wing tank corrosion, although the initial costs might be high. Estimates as high as one million dollars have been made for coating a T-2 tanker and annual maintenance painting touch-ups would be necessary also.

A number of coatings have been and are being tested in the wing tanks of the S.S. R. E. Wilson. These include vinylidene chloride-acrylonitrile, vinyl, epoxies, furane, zinc lead silicate and modified phenolic systems. Tests are being conducted using regular as well as KTA* panels and there are experimental applications upon local sections of piping. A number of failures have occurred, some of which have been because the coatings lacked chemical resistance. In other instances, failures of coatings otherwise suitably resistant and in some cases standing up well in the same service are ascribed to variables inherent in surface preparation and application. Typical failures involved loss of adhesion or subsurface corrosion.

On the basis of these tests and literature data, an experimental application of a vinyl system was made in the No. 6 port and starboard wing tanks in October 1953. Cranmer's objection to Butterworthing on vinyls did not apply in this case, since the coated tanks could be cleaned adequately by a cold wash, a detergent being added if necessary.

Although there was considerable difficulty in obtaining a good surface and in maintaining it between the sand-blasting operation and the application of the coating, the tanks were finally coated with what appeared to be a satisfactory film. There was some spray over-shooting, but a minimum of holidays. The condition of the finished tanks is shown in Figure 5.

These tanks performed beautifully for some three months. It was found that they could be gas-freed in less than half an hour by washing with cold water from a hand-hose.

After three months' service, some small holidays were evidenced by appearance of rust from the under-

* Kenneth Tator Associates, Coraopolis, Pa.
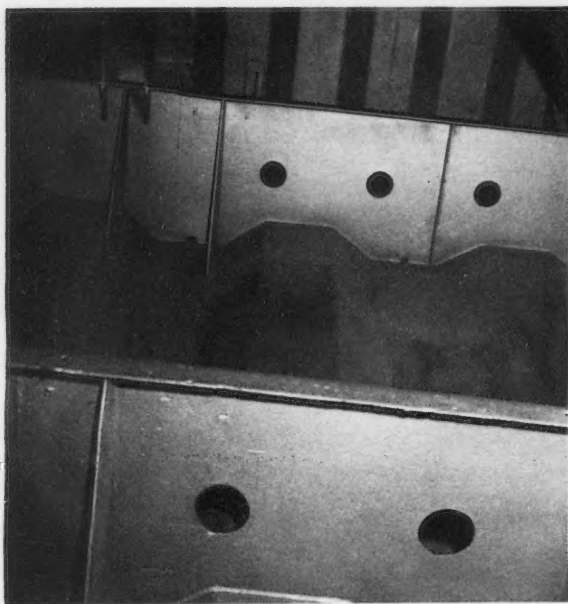
Figure 5—View of No. 6 port wing tank. Newly coated with a five-coat vinyl system.

Figure 6—Condition of coating in No. 6 starboard tank after six months' service. Note peeling and stripping.

lying steel. There also was some indication that the coating was losing its adhesion, or that it had not had good original adhesion locally. After six months' service, total failure of the coating by overall loss of adhesion was apparent upon casual inspection. The failures are illustrated in Figures 6 and 7.

It will be noted that there was no evidence of attack on the coating itself. In fact, the same coating on local piping sections is still performing adequately after more than a year. It is believed that the failure resulted directly from inadequate surface preparation of the badly corroded complex internal structure (Figures 8 and 9) under the conditions normally encountered in dry-docking.

Since the cost of this venture was well in excess of
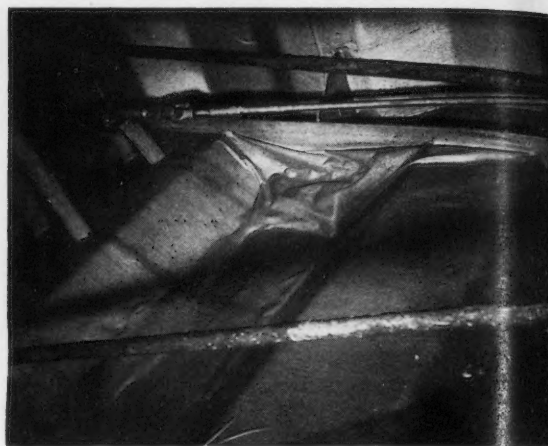
Figure 7—Coating failure in No. 6 tank showing absence of attack on the vinyl film with local loss of adhesion.

the estimated cost of $0.80 per square foot and since its economics are somewhat doubtful even if a successful application is achieved, it is believed that the present state of knowledge does not warrant this approach for the S.S. R. E. Wilson. It cannot be emphasized too strongly that failure of the vinyl system is wholly ascribed to surface preparation difficulties with the badly corroded surfaces in this twelve-year-old vessel. It is possible, for instance, that a successful and economical application might be made during the construction of a new vessel.

Dehydration—Removal of water from the environment and from the metal surface will effectively prevent corrosion. This approach is not applicable to ballasted tanks.

It has been noted already that corrosion during the cargo exposure is due to water at the metal surface, the hydrocarbons functioning only as a reservoir of dissolved oxygen. If the metal surface were desiccated prior to contact with cargo, this corrosion would be eliminated.

An attempt was made to dry the metal surface during hydrocarbon exposure in laboratory tests by additions of methanol or isopropanol to the cargo. Although additions of 0.5 percent of either alcohol will increase the solubility of water in refined hydrocarbons, no significant protection was achieved during tests of up to 1000 hours. This approach is of no apparent value.

Empty tanks may be protected by application of either desiccated air or desiccated flue gas. The latter technique entails the hazard of introducing carbon dioxide and sulfur compounds into the tanks, which might promote corrosion in the event of failure of the drying apparatus.[2]

The commercially available dehumidification systems operate by forced injection of air with very low relative humidity into the empty tanks, lowering the humidity below the critical point and effectively preventing corrosion. The equipment necessary to treat

eighteen wing tanks would cost in the neighborhood of $28,000 plus labor and overhead charges.

There was some question also whether the dehumidification systems could effectively dry the empty tanks during the relatively short duration of the voyage from the East Coast to the Gulf. Consideration of this method was abandoned when laboratory and field corrosion tests suggested that corrosion of empty tanks could be reduced drastically by other means (e.g., delayed Butterworthing or inhibited spray) at a lower cost.

De-Aeration—Removal of oxygen from the environment will prevent deterioration of steel effectively under conditions of aqueous or atmospheric corrosion.

There appears to be no practical method which will deaerate hydrocarbons. The addition of hydrazine, for instance, would involve handling hazardous material and costs would be prohibitive.

The atmosphere in empty tanks might be replaced with inert atmospheres, such as scrubbed flue gas. However, as previously discussed, this entails the possibility of increasing corrosion because it is difficult to exclude all oxygen and because sulfur compounds might be introduced into the environment. Such techniques have been used primarily over cargo to minimize the explosion hazard. Its potentialities for corrosion mitigation have not been defined quantitatively, nor are its economics now known.

Steel will remain bright indefinitely in oxygen-free sea water—in the absence of bacterial action—even when coupled to more noble materials such as millscale or copper alloys. If ballasted tanks were filled to the access hatches, it would be feasible to de-aerate the ballast by additions of sodium sulfite and the economics are inviting. Specifically, the solubility of oxygen in sea water (7.3 ppm at 20 C) requires about 56 ppm of sulfite for de-oxygenation. The addition of 100 lb. per wing tank would give a concentration of 70 ppm in the ballast, and the annual cost (at $.05/pound of sulfite) would be less than $1000.

Short-term laboratory tests and the initial field tests showed a very marked diminution of corrosion when the ballast phase was de-aerated. As the time of exposure was extended, however, the corrosion rates increased until they approached and sometimes exceeded the corrosion rate of the blank (Table 6). Similar effects have been observed with aliphatic chemical: sea water tests.

The loss of effectiveness of sodium sulfite additions with time was accompanied by the formation of black deposits on corrosion coupons. Initially, it was thought that this and the accompanying loss of protection was the result of the action of sulfate-reducing bacteria. In these tests, iron sulfides were detectable on the specimens and hydrogen sulfide was found in the water. Further, field tests persistently showed a rate of consumption of sulfite in excess of its stoichiometric relationship with the dissolved oxygen and this, too, was thought originally to be a consequence of consumption of the sulfite by bacteria. It was postulated that sulfite, as an intermediate compound in the reduction of sulfate, might be attacked preferentially by the anaerobic bacteria.
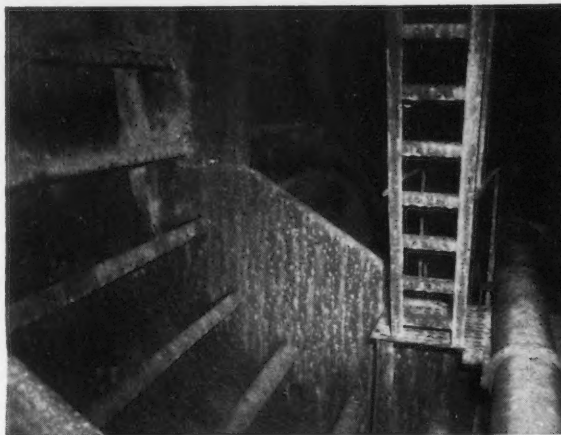
Figure 8—View of No. 6 wing tank before preparation for painting. Note complexity of structure.
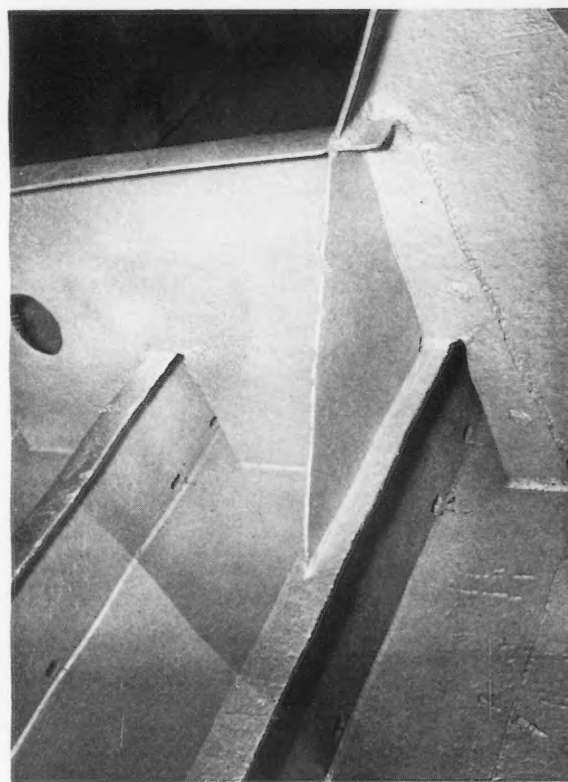
Figure 9—Paint application in No. 6 tank over pits, knife-edges and welds.

TABLE 6

Loss of Efficacy of Sodium Sulfite-Treated Ballast
(Inhibited Gasoline)

Alternate gasoline-ballast exposures

	336 Hr.	672 Hr.	1008 Hr.	1344 Hr.	1680 Hr.	2016 Hr.
Blank	.008	.006	.005	.005	.004	.004
70 ppm Na₂SO₃	.004	.004	.003	.004	.005	.011

TABLE 7

Ineffectiveness of Fresh Water Substitution in Alternate Gasoline-Wet Atmospheric Exposure with Inhibited Sprays

TREATMENT	Water	336 Hours	672 Hours	1008 Hours
None...............	Seawater	.012	.009	.008
None...............	Fresh	.012	.006	....
Polyphosphate.......	Seawater	.008	.007	.005
Polyphosphate.......	Fresh	.004	.004	.004
Soluble Oil..........	Seawater	.005	.006	.005
Soluble Oil..........	Fresh	.003	.004	.004

For all practical purposes, the influence of sulfate-reducing bacteria was eliminated, insofar as the corrosion was concerned, when analagous tests in either sterilized sea water or sea water treated with five parts per million of sodium pentachlorophenate continued to show loss of efficacy of the treatment with time.

It was concluded that the de-aeration of ballast by sulfite additions (or other techniques) would not prevent corrosion effectively under conditions of operation of the S.S. R. E. Wilson. Specifically, it is believed that under anaerobic conditions, chemical and physical changes occur in the otherwise protective scale and rust formations which permit continued high initial rates of attack upon subsequent exposure to aerobic conditions. The corrosion rate in any cycle using deaerated sea water is higher than that in the corresponding cycle with all phases aerated, presumably because of the quasi-protective nature of the corrosion products formed in the latter case. It was noted, for instance, that even with bactericides present, the rust scale formed during a cargo phase was reduced to lower oxides of iron during subsequent exposure to sea water containing residual sulfite.

Fresh Water—It has been suggested that the substitution of fresh water for sea water in ballast and cleaning operations would result in a marked diminution of corrosion. It is reported, for instance, that tankers operating on the Great Lakes suffer less attack than their sister ships plying salt water routes.

A change to fresh water ballast is impractical for ships operating between salt water harbors. However, the use of a fresh water wash, either as a substitute for the Butterworthing or as a rinse after cleaning, was not considered impractical. Fresh water was available at the Carteret terminal at a price of $.30 per ton and it was considered possible to load 3000 barrels into the forward deep tanks for such purposes. This would entail an expenditure on the order of $4000 annually.

Laboratory tests were initiated to determine the extent to which the use of fresh water in the Butterworthing stream would affect the overall corrosion rate. The tests also included the effect of certain inhibitors. A 336 hour test in a cycle simulating water-wet empty tanks gave a rate of .012 IPY regardless of whether the Butterworthing was done with salt or with fresh water. Table 7 illustrates that effectiveness of either soluble oil or glassy phosphate spray inhibitors is not significantly influenced by the salinity of the water except for initial exposure. The efficacy of the fresh water disappears with time.

In this regard, LaQue[11] has said: "Replacing salt water with a fresh water spray would have only a

moderate effect in reducing corrosion. The greatest benefit might come from the removal of hygroscopic salt particles which permit corrosion to occur at a lower relative humidity. This effect might not be noticed where the relative humidity is regularly high or where the surfaces are frequently wet with condensate."

It should be emphasized that the cycle of exposure in these tests involved no exposure of the steel to salt water in the tests in which fresh water was used. The fresh water replaced the sea water in its entirety. Similar results were obtained in tests in which the specimens were rinsed with fresh water after Butterworthing.

It is concluded that the use of fresh water on the S.S. R. E. Wilson would not significantly affect the overall rate of corrosion in clean service.

It might be suggested that the reported corrosion rates on tankers in fresh water service may be more profoundly affected by operational variables (e.g., the ballast requirements or the number, kind and frequency of cleaning operations) or by environmental factors (e.g., water temperature, atmospheric temperature, relative humidity and other meteorological conditions) than by the salinity of the water involved in the service.

Cathodic Protection—Cathodic protection is the protection of steel in an electrolyte by the application of a direct current from an external source in a direction opposite to that normally engendered by the corrosion process. This may be accomplished either by the use of sacrificial anodes (e.g., zinc or magnesium) or by applying a direct current from a battery or rectifier through inert anodes (e.g., graphite or a high silicon cast iron).

There is no question that such an approach is often a practical and economical solution in problems involving corrosion in aqueous media. Its application to the problem of tanker corrosion has been discussed in detail in the literature.[4, 12] However, while the anodes are effective during exposure to sea water, there was some question as to the degree of carry-over to other phases of exposure in various types of operational cycles.

Application of cathodic protection by means of a magnesium anode installation was the first suggested approach to the wing tank corrosion problem on the Wilson.

A trial installation of anodes was made in the No. 3 port and starboard wing tanks in May 1952 and evaluations of their merit have been made continuously since. The installation consisted of 50 fifty-pound anodes per tank. With a current output estimated at five amperes per anode and a favorable distribution of current, a current density of 15-20 milliamperes per square foot may be anticipated. This is in excess of the current density of 5-10 milliamperes per square foot normally required to polarize steel in sea water under relatively quiescent conditions. A view of the new anode installation is given in Figure 10.

The No. 3 tanks originally were restricted to ballast duty in order to get an appraisal of the anode effec-

Figure 10—

tiveness
shows t
Weight
years of
tioned t
extent of
with sea
cargo. |
adjacen
of an ele

Field
showed
the dura
the tank
some 40
gree of
when a
cause th
cent of

These
tests, |
ladders
the effe
amps/s
gasolin
It had
formed
would
and atn
quency
conside
vent fo
was fu
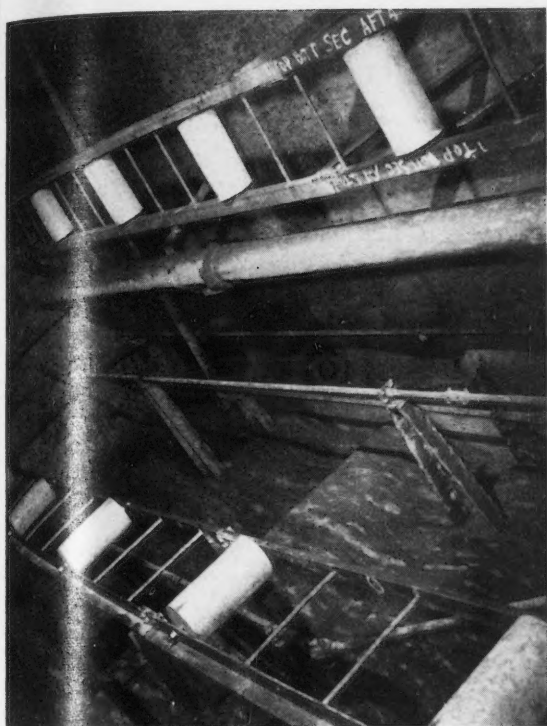
Figure 10—View of new magnesium anode installation in No. 3 starboard tank.

Figure 11—Condition of anodes in No. 3 starboard tank after two years' service. Note sporadic calcareous deposits.

Figure 12—View of corner of No. 3 starboard wing tank showing the exceptional calcareous deposit found in this localized area.

tiveness within a reasonably short time. Figure 11 shows the used anodes after two years service. Weight loss was such that two and one-half to three years of life might be anticipated. It should be mentioned that magnesium is expected to corrode to some extent during the cargo leg, because it would be wet with sea water and oxygen would be available in the cargo. However, such corrosion would not protect adjacent structural members because of the absence of an electrolyte.

Field tests on the S.S. R. E. Wilson originally showed a degree of protection roughly equivalent to the duration of exposure to sea water ballast. When the tanks were in alternate cargo-sea water service, some 40-50 percent protection was derived. The degree of protection was proportionally diminished when a rotating ballast pattern was employed, because the anodes were then in sea water about 25 percent of the time.

These first results were checked by field corrosion tests, by micrometer measurements on the anode ladders and by laboratory tests. Table 8 illustrates the effectiveness of cathodic protection at eight milliamps/sq. ft. in a 1000-hour laboratory test of alternate gasoline-sea water exposure.

It had been suggested that the calcareous deposit formed on steel by cathodic protection in sea water would effect a carryover of protection to the cargo and atmospheric exposures. It was felt that the frequency of cleaning operations demanded by toxicity considerations for the ballast would effectively prevent formation of an adequately protective deposit. It was further known that such deposits may not main-

TABLE 8

Comparative Efficacy of Cargo Inhibition and Cathodic Protection in Alternate Gasoline-Seawater Exposure

Duration, Hr.	Blank	Cathodic Protection*	Inhibition	Inhibition Plus CP
336	.008	.004	.009	.003
672	.006	.004	.005	.004
1344	.007	.005	.004	.004
2016	.006	.005	.004	.004

* 8 milliamperes sq. ft. cathode current density.

tain polarization of the underlying metal upon exposure to air. Humble[13] has cited an instance in which a calcareous deposit laid down at 125 milliamperes/square foot failed to maintain polarization of a steel plate exposed briefly to air during the tests.

Figure 13—Condition of calcareous deposit found behind supporting member. Note loose rust scale and gelatinous calcareous deposit.

Actually, an excellent tight calcareous deposit has been laid down in certain areas of the wing tanks (Figure 12). This type of coating might yield more effective protection if it could be obtained throughout the tanks. Some specimens in the No. 3 tanks for more than two years showed up to 70 percent protection, but results in the majority of the tests were poorer.

In certain areas, particularly those not reached by the Butterworthing spray, heavy but gelatinous deposits of calcium and magnesium salts are laid down. This is illustrated in Figure 13. This jelly-like material is probably ineffective in protecting the steel against corrosion in non-ballast exposures.

The theoretical basis for achieving an effective anode installation is still unknown. According to the literature, it is necessary to eliminate or minimize the Butterworthing operation if a "good" calcareous deposit is to be laid down. Experience in these tests, however, seems to indicate that un-Butterworthed areas do not receive the type of deposit necessary for adequate protection. It seems probable there is an intermediate condition between Butterworthing and freedom from Butterworthing which will allow the establishment of an adequate calcareous deposit under certain conditions of current density and duration of exposure to sea water.

A fixed ballast pattern, in normal operation, would leave the non-ballast tanks open to severe atmospheric corrosion. In the absence of counter-measures for the slack-tank corrosion, a rotating ballast pattern is necessitated, requiring anodes in all wing tanks of the S.S. R. E. Wilson. As compared with another ship using a fixed ballast pattern, with anodes in the ballast tanks only and these exposed to sea water half the time, it will be noted that an anode installation on the Wilson would involve twice as many anodes and their exposure to ballast only 25 percent of the time because of the rotating pattern.

Based on the installation in the No. 3 tanks, cathodic protection costs about $3000 per wing tank plus $1500 every two-three years for anode replacement. For eighteen wing tanks and a ten-to-twelve year life, this comes to an annual cost of $11,000 to $14,000 to achieve about 25 percent protection or slightly more.

It was long felt that this would be a "last-ditch" approach to be taken if a more economical method of alleviating ballast corrosion could not be found.

There is contradictory evidence, however, as to whether cathodic protection and cargo inhibition will supplement one another. In long-term laboratory tests, for alternate exposure to gasoline and sea water, it was found that either cargo inhibition or cathodic protection would give about 30 percent protection but that their effects were not additive. In other words, as shown in Table 8, no more protection was achieved by the joint use of cargo inhibition and cathodic protection at 8 ma/sq./ft. than by either treatment alone. Because the applied current was measured directly, it seems probable that alkalinity at the cathode interfered with operation of the cargo inhibitor rather than that the inhibitor restricted the applied current.

It must be admitted that field data do not seem to bear out these results, because there was evidence of cathodic protection in the tanks despite the presence of the inhibitor, but it would seem that further investigation is warranted.

It has been concluded that the cost of cathodic protection of the S.S. R. E. Wilson is not justified in the light of other applicable measures, some of which are mentioned below.

Inhibition—Inhibitors are specific in their solubilities and mechanisms and must be considered in relation to environments in which they are applicable. However, it was determined that results obtained from cyclic exposures were different from those obtained when a treatment was evaluated only in that phase in which one would normally consider it functional. A number of inhibitory treatments were considered and are discussed below under their appropriate media.

a. *Cargo*

The use of proprietary oil-soluble inhibitors has received considerable attention in relation to the tanker corrosion problem. There is evidence of the success of this approach as used by other operators.[3, 14]

This approach has been considered acceptable almost from the start of the Wilson investigation, because it was recognized that almost 50 percent of the corrosion occurs during the cargo leg. A long-chain carboxylic acid compound containing a phosphate grouping is available as a proprietary inhibitor for use at concentrations of 40-50 ppm. At a concentration of 50 ppm and a price of $3.66 per thousand barrels of cargo, the Wilson can be inhibited at an annual cost of $5500.

Table 9 shows efficiency of cargo inhibition in long-term laboratory tests under a variety of conditions. Table 9

Protection on the order of 30-50 percent appeared to be achieved always in long-term tests, the only variation being the ease with which the inhibitor became effective. Those testing techniques or conditions

which minimized high initial rates of attack allowed the inhibitor to become effective relatively early. The fact that the inhibition always became effective seems to indicate that the mechanism is intimately related to the presence and properties of protective corrosion products rather than to direct absorption on the metal surface.

There are no field test data available from the Wilson to verify the efficacy of the treatment, because there are no data from the pre-cargo-inhibition service. However, success of the laboratory experiments plus the reported success in the field by other operators indicates that the inhibitor will perform adequately at a reasonable cost. A 7-month field test by another operator reportedly showed 50 percent protection.

b. Ballast

It is agreed generally that inhibition of large amounts of ballast with conventional water inhibitors (e.g., chromates, nitrates, silicates, polyphosphates, etc.) is not feasible economically. For instance, although inhibition of one and a quarter million gallons of sea water with 1000 ppm of even so cheap an inhibitor as sodium nitrite would cost $10,000 annually, the water's salinity would require several times that concentration for effective treatment.

A further restriction, which is not recognized generally, is that imposed by toxicity requirements. It has been previously observed that clean ballast must be non-toxic. Therefore, those inhibitors which are inherently toxic (such as chromates) as well as those which operate outside the pH range from five to nine, are automatically excluded from consideration. It follows that toxic conditions in the inhibition of ballast can only be permitted in dirty ballast, i.e., under delayed Butterworthing conditions, where the inhibited water is discharged to the open sea.

It was hoped to find a cheap, non-toxic inhibitor which would be effective at concentrations on the order of 50-100 ppm.

A residue from pyridine production was known to be an effective inhibitor in pickling acids and in brines, but it was insoluble in sea water. Efforts to solubilize the residue by reaction with mineral acids gave some indication that the phosphoric acid reaction product might be an effective inhibitor. Results of preliminary tests usually were not reproducible and seemed to vary with the manner in which the ingredients of the inhibitor were added and reacted.

It was determined eventually that the orthophosphoric acid was itself the active ingredient. Table 10 illustrates the efficacy of orthophosphoric acid as an inhibitor in certain natural waters, in synthetic sea water and in certain distilled water solutions of inorganic chlorides. It appears to be effective in the range 50-100 ppm.

In long-term cyclic tests simulating the conditions in the S.S. R. E. Wilson under a rotating ballast plan, the phosphoric acid treatment did not maintain its efficiency, apparently due to the Butterworthing. However, it has done so in laboratory tests of up to 2000 hours in alternate sea water-atmospheric exposure. In another test of 1344 hours duration, it provided 60 percent protection in a cycle of inhibited

TABLE 9
Efficacy of Treatment of Cargo
With 50 ppm of an Oil-Soluble Inhibitor

	336 Hr.	672 Hr.	1008 Hr.	2016 Hr.
A. Alternate Gasoline-Ballast				
Blank	.006	.006	.006	....
Inhibited	.004	.004	.004	....
B. Alternate Heating Oil-Ballast				
Blank	.005	.005	.005	....
Inhibited	.004	.004	.004	....
C. Rotating Ballast (4-way cycle)				
Blank, gasoline	.005	.005	.005	....
Blank, heating oil	.005	.005	.005	....
Inhibited gasoline	.004	.003	.003	....
Inhibited heating oil	.004	.003	.003	....
D. Simulated Ballast Tank, Normal Operation				
Blank	.009	.007	.007	.008
Inhibited	.008	.006	.005	.004
E. Simulated Ballast Tank, Delayed Butterworth				
Blank	.003	.006	.006	....
Inhibited	.004	.004	.003	....

TABLE 10
Inhibition of Several Waters and Solutions
With 100 ppm of Orthophosphoric Acid

MEDIUM	Blank IPY	Inhibited IPY	Duration Hours
Seawater	.008	.001	100
Seawater	.004	.002	1000
Alternate seawater-atmosphere[1]	.008	.004	1000
Alternate seawater-inhibited gasoline[1]	.003	.001	1300
Brazos River water	.007	.001	100
.2 percent Calcium chloride[2]	.008	.004	100
3 percent NaCl, .5 percent MgCl₂, .2 percent CaCl₂[2]	.009	.004	100
Synthetic seawater[2]	.006	.001	100

[1] One week cycle.
[2] Distilled water solutions.

TABLE 11
Field Test Data in Wing Tanks
Illustrating low rates in slack tanks in absence of Butterworthing, fixed ballast pattern during these tests

Duration, Weeks	Ballast Tank	Slack Tank	Remarks
2	.006	.004	No Butterworth
4	.007	.005	No Butterworth
6	.006	.006	Butterworth resumed
8	.006	.006	
10	.006	.007	
12	.006	.008	
14	.007	.008	

gasoline-sea water. This potential application of orthophosphoric acid was considered to be of sufficient interest that a patent application has been filed.

Long term tests on sodium silicate, sodium nitrite and sodium tetraborate failed to indicate any significant protection at concentrations as high as 500 ppm.

It was concluded that there was no practical method for inhibiting ballast under the conditions of operation of the S.S. R. E. Wilson.

c. Atmospheric Corrosion

As has been noted previously, the corrosion rate in an empty tank is quite low provided the walls are not wetted between cargo and atmospheric exposures. This is illustrated in Table 5 under "Slack-Tanks." In original field tests to determine the efficacy of a magnesium anode installation in the No. 3 tanks, the adjacent No. 2 tanks were made permanent slack tanks and as such were restricted from both ballast and Butterworthing. Table 11 shows that the corrosion

rates in these tanks were actually lower than in the adjacent ballasted tanks until the Butterworthing was resumed.

It has long been recognized that corrosion is severe in empty tanks when they have become water-wet by any mechanism immediately prior to atmospheric exposure. Such a condition is inevitably encountered in normal operation of the S.S. R. E. Wilson, as previously described. It was therefore of considerable interest to develop a counter-corrosion measure to combat this exposure, which accounts for some 30 to 40 percent of the total corrosion in normal operation. (*cf* Table 3.)

A post-Butterworthing inhibited fresh water wash is reportedly effective in minimizing corrosion in empty tanks. Harden[12] has described one such system embodying a fresh water wash with an alkaline 5 percent sodium nitrite solution. Sudbury[1] has described a similar treatment which employs a soluble oil of the sodium aryl alkyl sulfonate type as the active ingredient.

Either system can be applied through the regular Butterworthing facilities or through a special piping and nozzle installation. In the latter case, the inhibitor costs are low because a relatively small volume of solution can be circulated from tank to tank. It has not been established definitely that such an installation, with its high initial cost, is economically superior to using the Butterworth equipment and washing with a larger volume of inhibited water made up in forward peak tank or cofferdam. A rough estimate for either installation might be six to eight thousand dollars annually.

Laboratory screening tests indicated that alkaline nitrite, alkaline chromate and soluble oil solutions in fresh water might be effective spray inhibitors against atmospheric corrosion. The use of the proprietary water-dispersable sulfonated oil was selected as showing the most promise economically and as being the easiest and safest material to handle and mix.

It was anticipated originally that the soluble oil inhibition would be handled as an inhibited fresh water spray installation. However, an estimate of the installation cost gave a figure on the order of $50,000 —plus a small annual expenditure for the inhibitor. The use of the Butterworthing equipment became of interest.

During the course of the investigation, it developed that although the soluble oil could not be dispersed in salt water even at concentrations of 0.1 percent, the material could be solubilized in fresh water and injected into the seawater, as a 20-25 percent fresh water solution, in such a quantity as to give the desired final concentration. Laboratory tests indicated that 1000 ppm of soluble oil was an effective spray inhibitor under these conditions.

In cyclic exposures of 1000 hours duration, the joint use of cargo inhibition, sodium sulfite in the ballast, plus a soluble oil-inhibited seawater Butterworth, held the corrosion of

clean steel coupons to less than .0005 IPY as compared with a blank of .0070 IPY for the untreated cycle.

Subsequent tests were conducted in a cycle of exposure simulating conditions in a tank restricted to slack duty only (i.e., inhibited cargo phase, Butterworth and atmospheric exposure). Duplicate test exposures were made for the first 1000 hours. At the end of this period, when all specimens were effectively scaled, the Butterworthing operation in one of the flasks was changed to embody inhibition with 1000 ppm of soluble oil-injected from a 25 percent fresh water solution into the sea water wash.

In the flask in which no inhibitor was used, the corrosion rate was .0070 IPY after two weeks' exposure, dropping to .0050 IPY at 1000 hours and so remaining for the duration of the 2000-hour test period. In the duplicate flasks, identical results were obtained for the first 1000 hours. At this point, the inhibited spray Butterworth was initiated in the second flask and the corrosion rate dropped to .0035 IPY at the end of the test period.

Use of an inhibited spray by the injection of a fresh water solution of soluble oil inhibitor directly into the hot sea water Butterworthing stream has been initiated on the S.S. R. E. Wilson and currently is under evaluation in field corrosion tests. Installation of a metering pump, mixing tank and requisite piping cost on the order of $5000 installed. The inhibition of 450 gpm of sea water with 1000 ppm of soluble oil worth $.075/lb., in amounts sufficient to Butterworth half the wing tanks (i.e., those discharged of dirty ballast) will add about $2000 annually.

It is anticipated that this treatment, in conjunction with the cargo inhibition, will decrease the overall rate of corrosion in the wing tanks approximately 75 percent.

Economics—It seems pertinent at this time to review the efficacy and cost of the individual treatments considered. From the previous discussion it will be seen that coatings, dehumidification and de-aeration cannot reasonably be considered. The choice then is narrowed to cargo inhibition, spray treatment and cathodic protection or some combination of these measures.

Protection to be derived can be estimated from the duration and severity of each phase of exposure in the cycle of operation and from the efficacy of the proposed countermeasures. An example of such a calculation is given in Table 12.

TABLE 12—Calculation of Effectiveness of Counter Corrosion Treatments

Conditions: Four-way cycle as of a rotating ballast plan, with dirty ballast discharged at start of ballast leg, i.e., slack tanks are water-wet.

Exposure	Severity	Duration Percent	Penetration[1]	Treatment	Efficacy Percent	Penetration Inh.
Wet Atmos	.010	25	.0025	Inhibited Spray	90	.0003
Gasoline	.008	50	.0040	Inhibitor	90	.0004
Ballast	.005	25	.0013	None	0	.0013
Pen IPY	....	..	.0078	....	..	.0020

Percent Protection = (.0078—.0020) x 100/.0078 = 70 percent[2]

[1] Corrosion without treatment.
[2] Note: This is maximum protection to be derived from combined cargo inhibition and spray treatment

An estimate may be made of the future costs of repairs in the total absence of countermeasures and of the gross annual savings for each increment of corrosion protection. As a first approximation, it has been calculated that each percent of corrosion protection for the S.S. R. E. Wilson is equivalent to a gross annual saving of $1000.

For normal operation in a rotating ballast pattern, the following cost data have been derived—

a. Cargo Inhibition—50 ppm of inhibitor
$3.66/1000 bbl. x 64,000 bbl. x 23 trips/yr. = $5400/yr.

b. Inhibited Spray—1000 ppm soluble oil in Butterworth
$69/trip x 23 trips/yr. = $1600/yr. plus $5000 initial installation, or $2100/yr. for 10 year write-off.

c. Cathodic Protection—
Initial installation, 18 tanks
18 x $3000/tank   = $54,000
Anode replacement at 3,6 and 9 years.
18 x $1500/tank x 3 = $81,000
                       54,000
                     ————————
                      $135,000

or $13,500/yr. for 10 year write-off period.

Assuming that any given measure is 90 percent effective in the environment in which it is applicable, which assumption is in line with both laboratory and field corrosion test results, the several treatments may be compared as follows:

Treatment	Percent Protection	Annual Cost
Cargo inhibition	45	$ 5,400
Inhibited spray	30	2,100
Cathodic protection	15	13,500
Cargo inhibition plus inhibited spray	75	7,500
Cathodic protection plus inhibited spray	45	15,600
Cathodic protection plus cargo inhibition	60	18,900

It is evident that the combination of cargo inhibition and inhibited spray is the logical choice for the conditions of operation for the S.S. R. E. Wilson.

It is believed that the delayed Butterworthing technique is impractical because of the objections previously discussed. However, a calculation similar to the above will select cargo inhibition over cathodic protection even for a fixed ballast pattern, in which the cathodic protection costs are reduced because of the lesser number of wing tanks carrying the anode installation.

It is estimated that the 75 percent protection anticipated from the combined cargo inhibition and spray treatment is equivalent to a gross annual saving of $75,000. The net annual saving will be of the order of $65,000.

Conclusions—Under the conditions of operation of the T-2 tanker, the S.S. R. E. Wilson, the following conclusions may be drawn from the data at hand.

1. The annual direct costs of corrosion will be of the order of $125,000 per year during the next 10-12 years.

2. The severity of corrosion is a function of the operating conditions.

3. The total corrosion effects and the appropriate remedial measures are profoundly affected by variations in the distribution of ballast, its toxicity requirements as regards marine life and the frequency and timing of the cleaning operations.

4. The most economical and practical approach to the problem consists of a rotating ballast pattern and the joint use of cargo inhibition and an inhibited sea water spray.

5. A net annual saving on the order of $65,000 is anticipated.

6. An extensive field test program is required to evaluate the effectiveness of the proposed treatments.

7. The line of reasoning and certain of the data, but not necessarily the conclusions, should be applicable to other tanker ships.

8. Extensive laboratory and field corrosion tests under a wide variety of conditions will be required before knowledge of the mechanisms of tanker corrosion—and of the appropriate counter-corrosion measures—will be complete.

Acknowledgments

References

1. J. D. Sudbury, D. A. Shock and F. W. Mann. *Corrosion*, **10**, No. 8, 253 (1954).
2. William B. Jupp. *Trans. Soc. Naval Architects and Marine Eng.*, **60**, 382-441 (1952). *Corrosion*, **9**, No. 11, 388 (1953).
3. J. V. C. Malcolmson, W. S. Quimby, Gwendolyn D. Pingrey and J. C. D. Osterhout. *Indem. Corrosion*, **9**, No. 11, 395 (1953).
4. A. B. Kurz. *Idem. Corrosion*, **9**, No. 11, 400 (1953).
5. A. Wachter and S. S. Smith. *Ind. and Eng. Chem.*, **35**, No. 3, 358 (1943).
6. J. C. Hudson. The Corrosion of Iron and Steel, p. 66, D. Van Nostrand Co., Inc. (1940).
7. F. N. Speller. Corrosion—Causes and Prevention. McGraw-Hill Book Company, Inc. (1951).
8. C. P. Larrabee. *Corrosion*, **9**, No. 8, 259 (1953).
9. H. H. Uhlig. Corrosion Handbook, p. 140, John Wiley and Sons, Inc. (1948).
10. W. W. Cranmer. *Corrosion*, **8**, No. 6, 195 (1952).
11. F. H. La Que. *Corrosion*, **9**, No. 11, 417 (1953).
12. G. B. Harden. *Proc. of the Third World Petroleum Congress*, Section VIII. E. J. Brill, Leiden (Holland), (1951).
13. H. A. Humble, The Dow Chemical Company, Private Communication.
14. Pan-American Refining Company, Private Communication.

Any discussions of this article not published above will appear in the December, 1955 issue.

Valves for Corrosive Fluids*

*By E. G. HOLMBERG**

THE PURPOSE of this article is to present information that will be of assistance to engineers endeavoring to recommend valves required to control the flow of corrosive fluids. It is written to satisfy numerous requests for information that can be passed on, especially to young engineers who have not had an opportunity to develop an experience background upon which they can rely when called upon to make these important recommendations.

When proper consideration is given to the 1) alloy selection, 2) effect of various corrosion processes, and 3) design for a particular set of service conditions, it is possible to write a specification for valves that will insure virtually maintenance-free service for many years. Proper consideration of these factors for all process equipment, as well as valves, will appreciably decrease the wasted manpower and lost materials incurred in many industrial installations.

Alloy Selection Methods

The sources in descending order of reliability from which data can be obtained (in the absence of directly applicable experience) for making an alloy recommendation can be listed as follows:

a. Corrosion tests conducted within vessels or solution lines of a full-scale operating unit.
b. Corrosion tests conducted within a pilot plant built to study the process characteristics.
c. Laboratory corrosion tests conducted in synthetic solutions and in equipment designed to reproduce or approximate conditions that will be encountered in a full-scale unit.
d. Corrosion test data available for materials used to handle solutions of a similar or preferably identical composition, at pressures, temperatures and velocities comparable to those that will exist within the the unit.

Obviously, if a chemical process is entirely new, representing an improvement over some previously employed process, or is designed to make an entirely new product, one of the last three methods designated will be employed for selection of the proper materials of construction. When it is necessary to select alloys for the construction of a new operation by one of these three methods, experience has indicated that corrosion tests should be conducted after the plant starts producing to determine the accuracy of the alloy selections and also to evaluate other less expensive alloys. Frequently, when first starting a new unit, there is a period during which operating "bugs" must be worked out. Unless it is desirable to obtain data for the metal loss suffered by the equipment during this period, corrosion testing should

Abstract

Methods are given whereby valves for control of corrosive fluids may be selected. Means of selecting suitable alloys are described, including laboratory and in-service tests, analogies of resistance through consideration of minor constituents and experience in actual plant service. Case histories of valve failures from corrosion are given and analyzed.

Detailed consideration is given to the design of valves and their component parts with recommendations concerning approved designs suitable for certain classes of service. The several kinds of flanged connections are described and their good and bad features analyzed. Details of internal construction that should be taken into account are itemized. Several valve standards are considered with respect to their applicability to corrosive services. The author reports it is the intention of the Manufacturers Standardization Society to develop standards for valves required to handle corrosive liquids at pressures over 150 psi.

be delayed until smooth unit operation has been achieved.

In Figure 1 is shown a corrosion test rod assembly which has been used successfully to obtain data under actual plant operating conditions. Because this assembly is installed within a solution line the specimens are exposed to the effect of velocity, as well as solution corrosivity. Dimensions of the ring shown at one end conform to those given in ASA Standard Practice B16.5, 1953, for the raised face of pipe flanges. As is indicated, the assembly is held in place by securing the ring, with a gasket on either side, between mating flange faces. A normal exposure period is usually 60 days. At the end of this time the assembly is removed and disassembled. The specimens are carefully cleaned and re-weighed. Penetration rates are then computed from weight loss, exposure hours, exposed area and specific gravity. For valves to provide a long service life to a particular environment, it is desirable that they be constructed of a material that has a corrosion loss rate less than
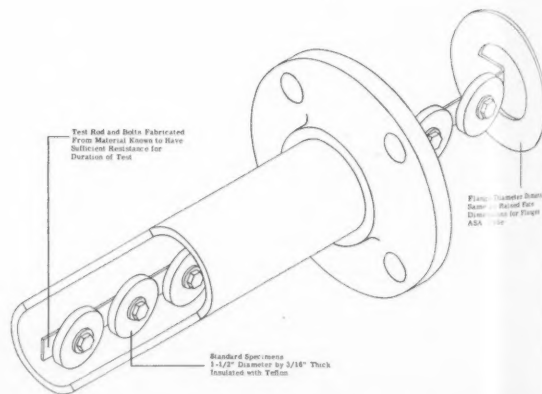
Figure 1—Device for in-service testing of materials in process line.

0.005-inch/year. Obviously, under some very severe conditions the economical alloy selection may be one that does not have this optimum resistance.

Corrosion Test Results

There are many so-called corrosion resistant alloys available today which have good engineering properties and are available in practically all forms (pipe, rods, sheets, castings). These are produced with composition limits which have been established by the American Iron and Steel Institute and the Alloy Casting Institute. Occasionally, it will be found that a modification in one of these analyses will appreciably change an alloy's corrosion resistance to a corrosive environment.

In Table 1 are tabulated data which show the effect of alloy modification on corrosion resistance to a solution of 56 percent sulfuric acid plus hydrocarbons at a maximum temperature of 176 F. The two commercial grades shown in these data are Aloyco 20 and Worthite. Under these conditions, neither alloy had the optimum resistance desired, although the corrosion rate computed for Worthite would indicate a somewhat better resistance than Aloyco 20. The data computed for Aloyco 38 would indicate that an increase in the molybdenum content of Aloyco 20 from 2.50 percent to 4.00 percent could be expected to increase the corrosion resistance to this environment approximately ten times. Corrosion data computed for another experimental alloy, Aloyco 35, showed this composition to be practically totally resistant. However, the data computed for Aloyco 37, which with the exception of the silicon percentage has a composition identical to Aloyco 35, indicated that increasing the silicon in the Aloyco 35 composition from 1.00 percent to 3.00 percent would result in destroying the corrosion resistance of this

composition to the exposure conditions. As all alloys of the type included in this test depend on the formation of a protective film for their corrosion resistance, it might be concluded that variations in film compositions were responsible for the results obtained.

Table 2 also shows the effect of an alloy modification on corrosion resistance to intermediate concentrations of acetic acid containing varying amounts of side reaction products, such as methyl formate, formic acid, etc. Aloyco 31 is the alloy of particular interest in this group and has the following nominal composition:

	Percent
Chromium	25.00
Nickel	10.00
Molybdenum	3.00
Manganese	0.75
Silicon	1.00
Carbon	0.07

It will be observed that Aloyco 31 is virtually completely resistant to three of the solutions and has a good resistance to the fourth. This alloy, being out of balance with respect to austenite and ferrite forming elements, has a two-phase structure (austenite and ferrite). Data obtained for tests conducted in intermediate concentrations of acetic acid (35 to 65 percent) at elevated temperatures would indicate that stainless Type 316 alloys, which contain a percentage of free ferrite, have a better corrosion resistance than the wholly austenitic structures.

In the use of such special alloy compositions as have been described, practical difficulties may be encountered. The alloy probably would be available only in the cast form and even then the number or size of castings required would have to justify pouring a full heat of the smallest capacity a particular foundry can produce. Many of these special compositions, it would be found, could be rolled into sheet or drawn into bars or tubes only with difficulty. Aloyco 31, because of its two-phase structure, is typical of such a composition. In this particular case it would be more economical to use wrought parts of Hastelloy C than to attempt to produce a small quantity of bars or tubes in this special composition.

TABLE 1—Corrosion Test Data

Solution: 56% Sulfuric Acid Sludge.   Temperature: 45-80 C (113-176 F).   Hours Exposure: 1104.

Alloy	Pen. Ipy.	PERCENT NOMINAL COMPOSITION							
		C	Cr	Ni	Mo	Cu	Mn	Si	Fe
Aloyco 20	0.0152	0.07	20.0	29.0	2.50	4.00	.75	1.00	Bal.
Aloyco 38	0.0013	0.07	20.0	29.0	4.00	4.00	.75	1.00	Bal.
Worthite	0.0094	0.07	20.0	22.0	2.50	1.00	.75	3.50	Bal.
Aloyco 35	0.0000	0.07	25.0	20.0	3.00	2.75	.75	1.00	Bal.
Aloyco 37	0.0296	0.07	25.0	20.0	3.00	2.75	.75	3.00	Bal.

TABLE 2—Corrosion Test Data

	SOLUTION PERCENT COMPOSITION			
Solution Number	1	2	3	4
Solution Components:				
a. Acetic Acid	45–50	45–50	45–50	33
b. Methyl formate, acetaldehyde, Methyl acetate, ethyl acetate, Acetone, methyl alcohol	5	15	....	....
c. Formic acid	2	2	4–6	1.5
d. Methyl acetate	....	....	1	....
Temperature	225	223	220	270
Hours Exposure	2328	3148	2544	5902
	Corrosion Data—Penetration, Inches Per Year			
Alloy:				
Aloyco 316	0.0362	0.0116	0.0539	0.0000
Aloyco 31	0.0000	0.0000	0.0073	0.0000
Admiralty	0.0153	0.0247	0.0000	Completely Corroded
Hastelloy C	0.0034	0.0051	0.0048	0.0016

TABLE 3—Corrosion Test Data

Solution: 1. 10% Sulfuric acid, no impurities.
           2. 10% Sulfuric acid, plus nickel sulfide impurities.

Temperature: 1. 225 F.
               2. 200 F.

Exposure Hours: 1. 240 (Five 48-hour exposures. New solution after each exposure).
                   2. 672 (Continuous).

Alloy:	PENETRATION RATES—Inches per Year	
	Exposure No. 1	Exposure No. 2
Aloyco 316	0.1500	0.0000
Aloyco 20	0.0355	0.0000
Aloyco 35	0.0762	0.0000
Hastelloy B	0.0024	0.7075
Hastelloy C	0.0504	0.0150

Solution Analysis

Chlorides as Cl_2 . . . . 210 ppm
Sulfites as SO_2 . . . . 472 ppm
Sulfates as SO_3 . . . . 232 ppm
Nitrates as NO_2 . . . . 15 ppm
Free S as S . . . . 2 ppm
Iron as Fe . . . . 28 ppm
Sodium as Na . . . . 45 ppm
Temperature . . . . 150-200 F
Exposure Hours 1320
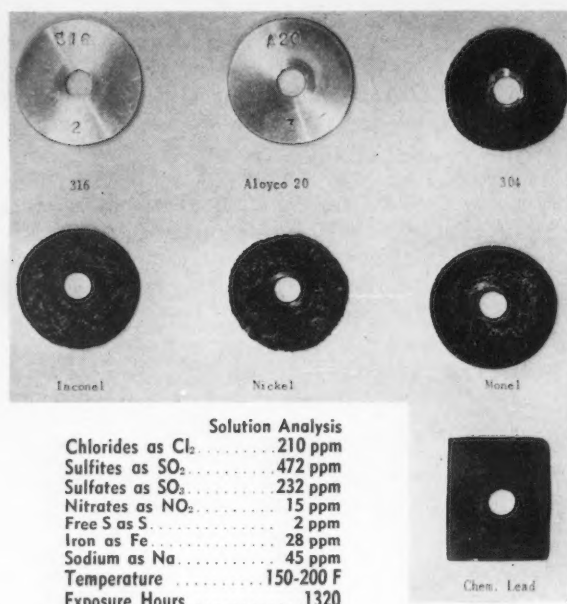
Figure 2—Corrosion test specimens after exposure.

Figure 3—Deposit attack.

Table 3 is of interest in that it emphasizes the importance of checking the effect of small percentages of impurities on corrosivity. The data for condition (1) were obtained from laboratory tests while those for condition (2) were obtained from plant tests. Upon reviewing these data it becomes clear that had results of Exposure (1) been used as a guide for alloy selection then Hastelloy B would have been selected. The table shows also that under plant conditions (Exposure 2) this alloy was most severely attacked. These tests indicate that nickel sulfide in 10 percent sulfuric acid will inhibit attack of the chromium-bearing alloys.

The data in Table 4 serve to emphasize the importance of molybdenum as an alloy addition. It will be observed that stainless Type 316 (2-3 percent molybdenum) was completely resistant to the solution conditions, while stainless Type 304, which does not contain molybdenum but otherwise has the same composition, showed a very high corrosion rate.

These data also show the importance of conducting adequate corrosion tests in that otherwise Aloyco 20 may have been selected for the service. If it had been, a premium alloy would have been chosen for a service in which it actually is not required. Figure 2 shows the condition of the specimens after exposure.

Plant Experiences

Figure 3 shows a valve gate disk that had been in sulfuric acid sludge service in an oil refinery. During most of its service life, the valve had been closed and, during this time, sediment accumulated in the corner formed by the junction
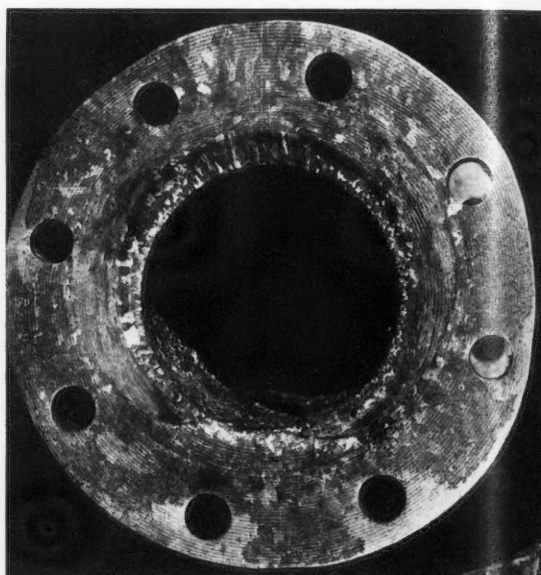
Figure 4—Effect of crevice corrosion.

TABLE 4—Corrosion Test Data

Solution:

Chlorides as Cl_2 . . . . . 210 ppm   Nitrates as NO_2 . . . . 15 ppm
Sulfites as SO_2 . . . . . . 472 ppm   Free S as S . . . . 2 ppm
Sulfates as SO_3 . . . . . . 232 ppm   Iron as Fe . . . . 28 ppm
Sodium as Na . . . . 45 ppm

Temperature: 150-200 F.

Exposure Hours: 1320

ALLOY	Pen. Ipy.	PERCENT NOMINAL COMPOSITION								
		C	Cr	Ni	Mo	Cu	Si	Mn	Pb	Fe
Aloyco 304	0.2038	.04	19.00	10.0	. . . .	. . . .	.90	.75	. . . .	Bal.
Aloyco 316	0.0000	.04	19.00	11.0	2.50	. . . .	.90	.75	. . . .	Bal.
Aloyco 20	0.0000	.04	20.00	29.0	2.50	4.00	.90	.75	. . . .	Bal.
Nickel	0.1594	.35	. . . .	Bal.	. . . .	. . . .	1.50	.80	. . . .	.50
Inconel	0.1335	.10	13.5	Bal.	. . . .	.30	1.00	.75	. . . .	6.00
Monel	0.0398	.10	. . . .	Bal.	. . . .	30.0	1.25	.75	. . . .	1.00
Mild Steel	Lost	.15	. . . .	. . . .	. . . .	. . . .	. . . .	.25	.80	. . . .	Bal.
Chem. Lead	0.1265	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	99.9+	. . . .
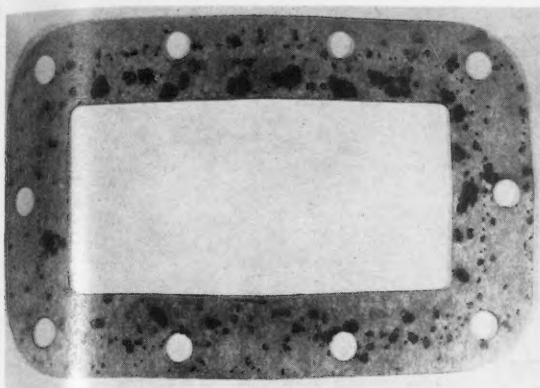
Figure 5—Pitting corrosion, Type 304 valve bonnet gasket.

of the disk and the circumference of the waterway. The metal loss which occurred below this deposit is referred to as deposit attack. It is a form of the solution cell or crevice-corrosion type phenomenon.

Figure 4 shows the end flange of a gate valve which, because of gasket design, was exposed to crevice corrosion. It will be observed that the ID of the gasket used on this end flange was cut to conform to the OD of the pipe. The crevice thus formed permitted sediment and corrosion product to accumulate between the faces and crevice attack to progress. Although there may be a tendency toward this type failure at connections under some solution conditions, its severity can be materially reduced, or in many cases eliminated, if gaskets having an ID to conform to that of the pipe are used.

Figure 5 is an example of another type of failure sometimes found at gasket joints of stainless steel valves. It will be found more severe when the alloy does not contain molybdenum. The gasket shown was taken from a stainless Type 304 valve which had not been in service. An analysis of the gasket material showed chlorides, sulfates and some free iron. Each of the areas which appears black in the photograph had the characteristic iron-rust color. The metal surfaces opposite these areas were pitted to varying degrees, some as deep as $\frac{1}{16}$-inch.

Design of Valve Components

Following are described each of the components used in the assembly of corrosion resistant valves. Also presented are reasons for selecting specific designs.

1. *Valve Body*

a. **General.** The valve body can be considered as the "heart" of a valve, as its performance frequently will determine either the success or failure of a particular design. For valves that will be required to handle a wide variety of corrosive solutions, the body should be provided with suitable end connections, bonnet connection and seating surfaces that will not, because of design, aid a particular corrosive process which the solution conditions may tend to promote. The wall sections of the body should be of ample thickness to provide adequate strength, which will insure freedom from dimensional changes when subjected to: 1) the maximum pressure for which the valve is designed, 2) normal line stresses, and 3) normal stresses imposed when tightening the valve disk or disks into, or opening from, the closed position.

b. **Threaded Connections.** Threaded connections have not been entirely successful as a dependable leak-proof method for the assembly of valves into a piping system that will convey a corrosive solution. Threaded connections leave a crevice on the inside of the pipe where crevice-corrosion can occur. Should the solution being handled promote this form of attack, the connection eventually will leak and be weakened by metal loss. Seal welding will serve to improve the performance of these connections by preventing air and moisture from the atmosphere intermixing with solution that may work its way between the threads.

Many corrosion-resistant alloys have a strong tendency to gall when in bearing contact. This is particularly true for all grades of austenitic stainless steels. When threaded connections are used for the assembly of equipment fabricated from these alloys, difficulty frequently is encountered in attempting to get complete thread engagement, because the threads will gall before this is accomplished. To minimize galling, it is mandatory that threads cut in these materials have the proper dimensional tolerances and be free from rough edges and tears.

Most so-called "pipe dopes" have been only partially successful as an aid in obtaining a tight seal and overcoming the galling tendency. Some have insufficient anti-friction properties, so that even when "dopes" are used, galling will occur. Others, although being good anti-friction compounds, leave a film between the threads that is not resistant to the corrosive to be conveyed and when this material is decomposed, a loose and leaky connection results. The writer's company's experience shows the most successful anti-friction lubricant for threaded connection of austenitic stainless steels is molybdenum disulfide, either as a powder or a paste.

Considering these factors, it also can be concluded that the male-female threaded connection for securing the valve bonnet to the valve body may likewise be considered an undesirable design. Should it be considered practical because of size to secure the bonnet by means of a threaded connection, the union-ring bonnet construction is preferred. The threads of this type connection will not be directly in contact with the process solution. Figure 6 shows the male-female bonnet connection and Figure 7 shows the union-ring design.

c. **Flanged Connections.** Flanged connections have been found most satisfactory for valve bonnets and piping connections. Some designs are preferred, while others are questionable. A tabulation according to these classifications is as follows:

Preferred Designs—1) Plain Face, 2) Raised Face, 3) Large Male-Female, 4) Small Male-Female, 5) Lapped.

Questionable Designs—1) Large Tongue-Groove, 2) Small Tongue-Groove, 3) Ring Joint.
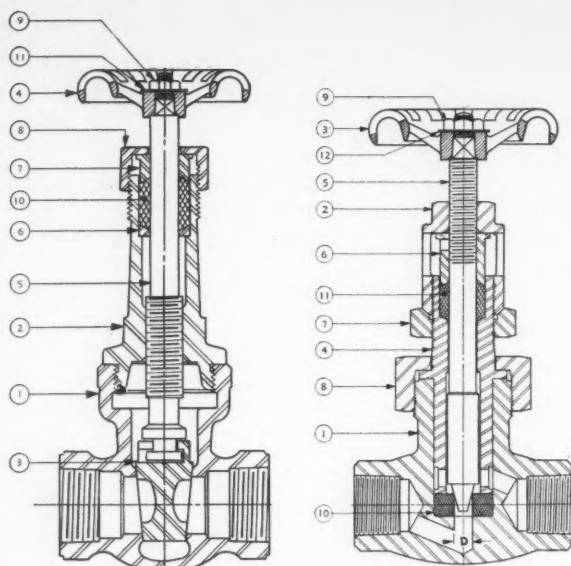
Figure 6 (Left)—Gate valve. Identification of parts: 1. Body. 2. Bonnet. 3. Wedge. 4. Handwheel. 5. Stem. 6. Packing ring. 7. Gland follower. 8. Packing nut. 9. Wheel nut. 10. Packing. 11. Identification plate.

Figure 7 (Right)—Needle valve. Parts identification: 1. Body. 2. Packing nut. 3. Handwheel. 4. Bonnet. 5. Stem. 6. Gland follower. 7. Packing nut lock nut. 8. Union ring. 9. Handwheel nut. 10. Seat. 11. Packing. 12. Identification plate.

Figure 8—Preferred and questionable flange designs.

Figure 8 shows the constructions of these flange designs.

Qualifications for each design can be summarized as follows:

1) *Plain Face:* A soft compressible sheet gasket material (asbestos, rubber, Teflon, etc.), cut to cover the entire facing between the flange ID and OD is used to seal the joint between the flanges of this design. Because of a relatively low compressive force per unit gasket area, as compared to other designs, full-face metal-jacketed or spiral-wound gaskets are not successful when used with this type. Provided a gasket material resistant to the corrosive is employed and the gasket ID and pipe ID are the same, flanges of this design provide a smooth, continuous waterway connection. This freedom from crevices or pockets, in which sediment or corrosion products may accumulate to cause concentration cell corrosion, is a necessary feature.

The gasket surface of this design is machined with a phonographic finish having serrations appoximately .007-inch deep. This also will be true for flange facings of subsequent designs when soft gasket materials are used.

2) *Raised Face:* Flanges of this design have all the merits of the "plain face" flange, plus the added advantage of being suitable when employing relatively hard gasket materials. When properly tightened, the compressive force developed per unit gasket area will permit the use of metal-jacketed or spiral-wound gaskets between flange faces machined with a smooth finish.

3) *Large and Small Male-Female:* The remarks made for "plain face" and "raised face" flanges also apply to flanges of these designs. From a safety standpoint for some high-pressure conditions these flanges would probably be preferred, for if a gasket failure occurs because of decomposition, there would be only a slight possibility that a high velocity stream would flow directly from the flange joint. It will be observed that when a gasket of proper thickness is used the contact surface of the male flange will be below the outer face of the female flange. Also, it is obvious that this construction will reduce the possibility of a gasket blowing out.

4) *Lapped:* The lapped flange with stub end will form a connection when bolted to another lapped flange with stub end, or to a raised face that will be practically identical to that formed by two raised-face flanges. Both hard and soft gasket materials can be used to seal the connection. A crevice will not exist at the joint when the gasket ID is cut to conform to that of the pipe.

5) *Large and Small Tongue Groove:* Gaskets of practically all types can be used with these flange designs. Although their construction will completely retain the gasket, they have the objection, when finally made up, of leaving a crevice or gap between the flanges of a width equal to the final compressed thickness of the gasket. For handling corrosive fluids, where it is known crevice-corrosion can develop, these flange designs should be avoided. For non-corrosive media at high temperatures and pressures,

RENEWABLE SEAT   INTEGRAL SEAT
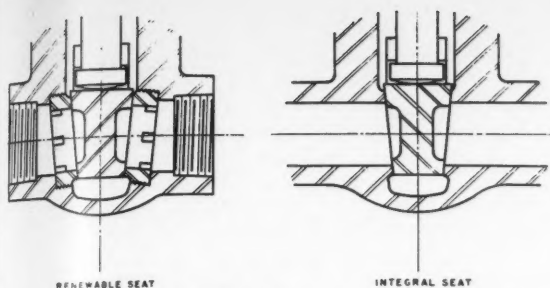
Figure 9—Renewable (left) and integral (right) seat designs.
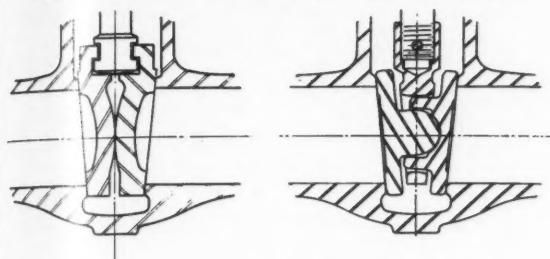
DOUBLE WEDGE   BALL & SOCKET WEDGE
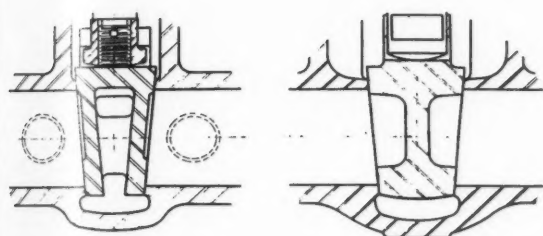
CORED WEDGE   SOLID WEDGE

Figure 10—Principal gate valve disc designs.

in conjunction with the use of a metallic gasket, they should be quite satisfactory.

6) *Ring Joint:* Ring joint flanges were designed originally for application in high-temperature, high-pressure piping systems required to convey noncorrosive media. They are rarely used in low-pressure piping systems that convey corrosive solutions, because their application is limited to the availability of metal ring-gaskets of proper hardness and adequate corrosion resistance. Ring-joint flanges also have the objection of leaving a gap (where crevice-corrosion can occur) at the flange joint when finally made up. The width of this gap is an important consideration in the design of these flanges.

d. **Body Seats.** Valve bodies designed for corrosive applications have seating surfaces which are integral with the body. The mechanical desirability of the renewable seat ring design has been sacrificed in valves required to handle corrosive fluids, because corrosion resistance must be given preferred consideration. Renewable seat rings have been found undesirable because

1) Threaded connections in most corrosion resistant alloys will gall before the ring is tight.

2) The renewable feature frequently is lost because the ring cannot be removed without damage to the threads after the valve has been in service for some time.

3) It is difficult to be assured of having a joint that will be tight under all operating conditions, because the ultimate effect of pressure, temperature and the wetting or penetrating properties of various solutions cannot be successfully anticipated.

4) Failure of the valve to provide complete shut-off can result from corrosive action in the crevice formed between the seat ring and the body.

5) In corrosive applications, it is best to select one alloy which has the most satisfactory resistance.

6) When dissimilar alloys are in contact and exposed to some solutions that serve as electrolytes, corrosion of the less noble alloy will be accelerated galvanically.

Figure 9 shows the removable seat ring and integral seat constructions.

When solutions are handled which contain abrasives that cause scoring of the seating surfaces, the writer's company's experience would indicate that hard facing of these surfaces is not always the solution. Valves of the globe or "Y" design, having disks with Teflon inserts, have been found most satisfactory. Upon seating the disk of this design, the abrasive particles will imbed in the Teflon without causing either damage to the metal seating surface or inability to effect a tight closure.

2. *Valve Disks*

a. **Gate Valves.** The disk, gate or wedge in these valves can be either the two-piece or one-piece construction. There are two principal double-disk designs—the double wedge and the ball and socket wedge—used in valves required to handle corrosive fluids. Figure 10 shows these constructions. The double wedge is composed of two disks each having identical dimensions and shaped like a cupped hand. When installed, they are placed back to back so that the machined faces will contact the body seating surfaces in the closed position. A groove, at the top of each disk, is machined to fit a milled slot in the stem foot from which each is suspended. This design has the objection of being susceptible to wear at the stem connection and excessive wear will permit either one or both disks to become disengaged.

A disk design, which the writer believes to be better than the above, is the ball and socket type. One disk has a ball machined on the back, which, when in the assembled position, will fit into a socket machined in the back of the second disk. This design will permit considerable wear in both the disk holder and ball and socket joint without either disk becoming disengaged. It also has an advantage over other designs in that the disks are free to rotate and will not seat along identical surfaces upon repeated clos-

ure. Experience would indicate also that the ball and socket wedge has far less tendency to cause galling of the seating surfaces.

As also shown in Figure 10, the one-piece disk can be either a solid-wedge or cored-wedge design. As each of the body seats in valves employing wedges of this type is mostly commonly machined at an angle of 5 degrees to the vertical axis of the valve, disk faces are machined to form an included angle of 10 degrees. The solid wedge is used in valves required to handle solutions that do not have entrained solids which may settle in the pocket beneath the seating surfaces and thus interfere with full travel of the gate. The cored wedge, however, will perform satisfactorily when this pocket contains an accumulation of solids, because the two rather narrow lips at the bottom of the disk will cut into the solids and force them into the cored out area within the wedge. When the valve is opened, turbulence will wash away any solids the wedge may have retained. Both designs usually are provided with a "T" slot at the top to receive the stem that actuates the disk.

b. **Globe Valves—Angle Valves—"Y" Valves.** Globe, angle and "Y" valves are most generally designed to have the stem rotate when the handwheel is turned to perform either the closing or opening operation. As this action would result in galling of the seating surfaces if the disk were an integral part of the stem, the swivel disk design is used. These disks in valves constructed of austenitic stainless steels and other corrosion resistant alloys have been of various types; namely, the modified-plug, ball-plug, renewable-disk and "V" port-plug. The design and manner of seating for all four is shown in Figure 11. The disk of each design is secured to the stem by means of a swivel nut machined to fit over a shoulder at the stem foot. After complete thread engagement, it is important that the disk and swivel nut be pinned to prevent their coming apart while in use.

The seating surface of the modified plug is machined to form an included angle of 30 degrees and the seating area is reduced to approximately ⅓ of that for a full body seat. Experience has shown that this is more reliable in producing a consistently tight closure with a minimum of handwheel tightening.

The seating surface of the "ball plug" is machined on the radius of a sphere while the body seat is machined at an angle of 45 degrees. When the plug is in the closed position, line contact will be had around the seating surface. This usually is preferred for handling solutions having suspended crystal particles or that may tend to crystallize on seating surfaces.

In the "renewable disk" design various non-metallic materials, as well as soft metals, can be secured within the disk holder. Teflon, because of its outstanding resistance to a broad range of corrosives, has been found an excellent material for these disks. The renewable disk design will insure tight closure when handling solutions which contain entrained solids that tend to deposit on seating surfaces. Upon closing, solids will imbed in a soft disk

MODIFIED PLUG   BALL PLUG

RENEWABLE DISC   V-PORT PLUG
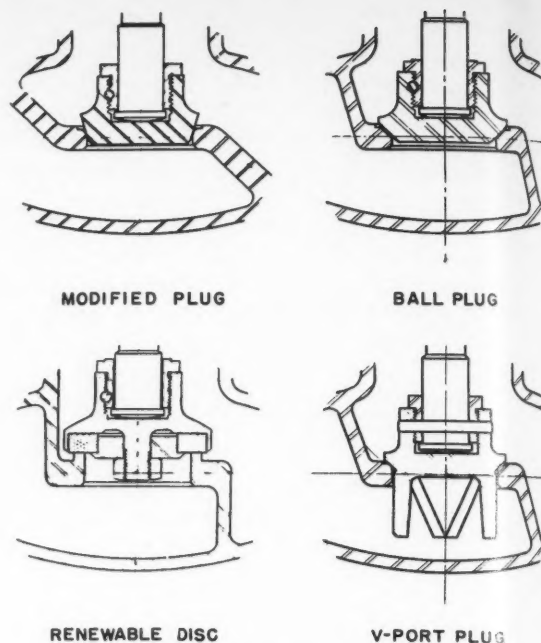
Figure 11—Principal globe valve disc designs.

material (Teflon, when it is used) and thus will not interfere with obtaining tight shut-off, as would be the case with metal-to-metal seating. This design also will permit use of less expensive alloys which have a borderline corrosion resistance to the fluid being handled. An etched condition of the body seat will not interfere with obtaining a tight shut-off, because the roughened surface will imbed in the Teflon disk. It is also an excellent design for vacuum service.

Still another design globe valve that varies somewhat from the standard type is the one employing a "V"-port disk, which is an adaptation of the type used in most motor operated flow control valves. The seating surfaces of the "V"-port disk are machined at an angle of 45 degrees. As shown in Figure 11, the disk is constructed with a skirt, in which there are "V"-port openings that permit closer fluid control than can be obtained with globe valve disks of conventional designs. As the fluid passing the disk would cause it to rotate at a relatively high velocity, valves of this design are constructed with a non-rotating rising stem, which will permit pinning the disk to the stem.

c. **Needle Valves.** Conventionally designed needle valves, having a disk or needle point integral with the stem, have not been entirely successful when used to handle corrosive fluids and when constructed of corrosion resistant materials that tend to gall. The relatively short service life of these valves has been found to be principally the result of galling at the seating surfaces. The writer's company has discovered, as shown in Figure 7, that this weakness in needle valves can be eliminated by employing a corrosion resistant soft-seating material, such as Teflon, which will serve to protect the stem seat.

d. **Check Valves.** The most common type of valve

employed to control the directional flow of fluids in piping systems is the swing-check valve. This valve is equipped with a single disk that is suspended by means of an arm secured to the valve cap or at a suitable point within the valve bonnet. The disk is machined with a flat seating surface that contacts a similar surface, machined at an angle, usually 5 degrees, around one waterway opening into the body area. Should a tighter closure be desired for some conditions than can be obtained with metal-to-metal seating, the renewable-type disk can be used.

The second most popular check valve is the lift type, the use of which is usually confined to small diameter piping. The disk in this valve has a stem as an integral part. The stem, which passes through a suitable sleeve in the bonnet, controls the movement of the disk and insures proper seating. The most satisfactory seating surface will produce line contact.

The ball-check is another type; however, it has not been extensively used for controlling the flow of corrosive fluids as balls are available in only a very limited number of alloys. Glass balls, which would be resistant to a wide range of corrosive fluids, have the weakness of cracking or chipping easily.

e. General. Special valves, such as flush-bottom tank valves, sampling valves, gauge-glass valves, jacketed valves, etc., will have employed in their construction disks of one of the foregoing designs.

For good performance of all valve disk designs made from corrosion resistant alloys, special machining techniques must be employed to obtain surfaces having a high degree of dimensional accuracy. Seating surfaces must be machined extremely smooth, free from scores and irregularities that may cause galling or interfere with obtaining complete shut-off.

3. Valve Stems

a. Design Details. The modified acme thread has been adopted as standard for stems machined from austenitic stainless steels and other high alloys.

Most stem designs are provided with a shoulder that contacts a seating surface machined in the bottom of the bonnet below the packing gland. This will serve as a back seat when the valve is in the wide open position and will permit repacking of the valve while under pressure. The stem foot to which disks are secured is machined in various ways to accommodate the particular disk design.

b. Machining. Extreme care must be exercised in the machining of stem threads to produce surfaces that will be smooth and free from tears. The unthreaded portion of the stem, particularly the area that will comprise the packing travel, must also have a smooth finish (4-8 RMS) to insure obtaining a proper seal when in contact with the packing.

4. Valve Bonnets

a. Design Variations. Valve bonnets are of two principal designs: 1) inside screw, and 2) outside screw and yoke. The base of the bonnet is machined for either a 1) male-female connection, 2) union ring connection, or 3) flange connection.

b. Male-Female and Union Ring Bonnets. Bonnets having either the male-female or union ring bonnet connections usually have threads machined on the inside bore (inside screw) below the packing gland for controlling the stem movement. As these threads will be in contact with the solution and therefore subject to some metal loss because of corrosion, the inside screw design is not considered best suited for corrosive applications. Such a modification, however, as threading of the packing nut to place the packing between the solution and the stem thread, is quite an acceptable design (Figure 7).

As previously stated, the union-ring bonnet connection is preferred to the male-female design.

c. Outside Screw and Yoke Bonnet. The outside screw and yoke bonnet, with a threaded bushing at the top for actuating the stem and a flange at the base with a minimum of four bolts for securing the bonnet to the body, is preferred design for all valve types. The two bolt bonnet flange construction should be avoided because of the hazard that would be imposed should one bolt fail as a result of corrosion or defective material.

d. Packing Glands. Packing glands in all valve bonnets should have sufficient depth and diameter to permit installation of standard packings that will produce a tight seal at the temperature-pressure ratings for the particular valve design. Table 5 shows a relationship between the stem diameter, packing size and minimum contact length, which has been generally accepted as standard for corrosion resistant valves in the 150, 300 and 600 psi pressure classes.

e. Gland Plate and Follower. To be assured of straight downward travel of a packing follower, the two-piece gland plate and follower with a ball and socket connection between the two has been found a very satisfactory design. Should the gland plate of this design become cocked, because of uneven tightening on the gland bolt nuts, the force that could be applied will not be transmitted to cause excessive binding of the follower on the packing box wall or stem, as would be the case with the one-piece construction.

f. Bolting. Stainless Type 303 nuts with stainless Type 304 bolts are representative of the minimum alloy combination acceptable for bonnet and packing gland bolts and nuts. Because valve bolting is not directly in contact with the solution, bolts and nuts of these alloys have been found very satisfactory for practically all conditions. Some special applications require that more highly alloyed bolting materials be used.

TABLE 5—Packing Sizes
All Dimensions in Inches

Range of Valve Stem Diameter	Packing Size	Minimum Packing Contact Lengths for Primary Service Rating of		
		150 psi	300 psi	600 psi
Up to 15⁄32 inclusive	1⁄8	3⁄4	3⁄4	3⁄4
1⁄2 to 15⁄32 inclusive	3⁄16	1 1⁄8	1 1⁄8	1 1⁄8
9⁄8 to 1 inclusive	1⁄4	1 1⁄2	1 1⁄2	1 1⁄2
1 1⁄32 to 1 3⁄4 inclusive	5⁄16	1 7⁄8	1 7⁄8	1 7⁄8
1 25⁄32 to 1 7⁄8 inclusive	3⁄8	2 1⁄4	2 1⁄4	2 1⁄4

Valve Standards

1. *MSS SP-42*

The MSS SP-42 standard practice for flanged end valves in the 150 lb. class is the only existing standard specifically designed for valves to be used for the control of corrosive solutions. Dimensional data are shown in this standard for the following valve designs: Gate, Globe, Angle, "Y" Pattern Globe, "Y" Swing Check, Swing Check, Lift Check.

2. *ASA B16.10-1939*

Face to face dimensions for corrosion resistant flanged end valves having a primary service rating of 300 and 600 psi are in accordance with this standard for ferrous valves. The face to face dimensions for flanged end valves having a primary service rating of 150 psi are also shown in this standard for 2-inch sizes and above. Even though these dimensions for sizes through 12-inches are in agreement with MSS SP-42, the MSS SP-42 standard is more useful for this pressure class, because at this time it is the only standard which shows face to face dimensions for sizes ¼ through 12-inches. Reference to B16.10 for the 150 psi pressure class should only be necessary for sizes over 12 inches.

3. *ASA B16.5 - 1953*

Dimensional data for steel flanges and flanged fittings, as well as primary pressure-temperature ratings, are given in this standard.

When flat face flanges in the 150 psi pressure class are required for corrosion resistant valves, they usually are made in accordance with the MSS SP-42 standard. The B16.5 standard is used when facings other than plain face are desired for 150 psi class. The number of bolts, bolt hole diameters and diameters of bolt circles for 150 lb. flanges of the MSS SP-42 design will conform to this standard. The thickness only of MSS SP-42 flanges will be at variance.

This extra flange thickness required for the special facings of this standard will not change the face to face dimensions for 150 lb. valves as given in MSS SP-42. The extra metal is added to the back of the flange.

4. *API 600*

This standard is quite generally used for the production of corrosion resistant flanged end valves that are usually referred to as Class 300 and Class 600. The face to face dimensions and flange dimensions specified are in accordance with ASA B16.10 and ASA B16.5. The minimum wall section thickness dimensions designated for valves of each pressure class usually will be greater than minimum metal thickness dimensions established in B16.5 for fittings of respective size and pressure class. The API minimum metal thickness represents the ASA minimum, plus an extra amount for corrosion allowance. In valves required to handle corrosive fluids, this added metal does not appear justified if the proper alloy selection is made. Valves in the 150 lb. pressure class contructed of austenitic stainless steels and other high alloys are rarely ever made to the specifications of this standard.

5. *General*

Ultimately, it is the intent of the Manufacturers Standardization Society to develop standards for valves required to handle corrosive liquids at pressure over 150 psi. This will eliminate the need for using existing standards that were designed primarily for valves required for non-corrosive services and, also, the necessity for taking exceptions to these standards so that the final valve design will perform satisfactorily when handling corrosive fluids.

From the foregoing it should be concluded that an understanding of the materials commonly employed to resist the action of corrosive fluids, as well as the mechanics of various corrosion processes, is important when developing valve designs for controlling the flow of corrosive process solutions.

Any discussions of this article not published above will appear in the December, 1955 issue.

Technical Committee Activities

High Temperature Sulfide Corrosion Explored

Austenitic Stainless Stress Cracking Study Approved

The Managing Committee of the Technical Practices Committee has announced the tentative approval of formation of a new Unit Committee under Group Committee T-5. The committee will study stress cracking of austenitic stainless steels.

L. M. Rogers of Carbide & Carbon Chemicals Company in Texas City has been appointed temporary chairman of the committee. It was through Mr. Rogers' efforts the committee was formed.

The committee has been tentatively designated T-5E on Stress Corrosion Cracking of Austenitic Stainless Steels. An organizational meeting will be held during the South Central Region meeting in Houston. The meeting time has been set at 2:00 p.m., October 18, in the Castilian Room C at the Shamrock Hotel.

It has been suggested the committee might start a study of case histories of failures and/or a review and study of laboratory techniques concerning stress cracking of the austenitic stainless steels.

All NACE members interested in becoming a working member of this new committee are invited to attend the organizational meeting.

Burton Is Nitric Acid Task Group Vice-Chairman

W. H. Burton, General Chemical Div., Allied Chemical and Dye Corp., Camden, N. J. has been elected vice-chairman of Task Group T-5A-5 on Nitric Acid.

He received his ME and MS degrees from Stevens Institute, Hoboken and is a licensed professional engineer in the state of New Jersey. Currently he is Material Consultant with General Chemical Div., of Allied Chemical and Dye Corp. During his 22 years with General Chemical he has held several supervisory engineering positions.

Besides membership in T-5A-5 he also is a member of T-5A-6 on Hydrofluoric Acid. He is a member of ASTM Committee C-3 on chemical resistant mortars and of the High Alloy Steel Committee of the Welding Research Council of the Engineering Foundation.

Bibliographies Completed on Corrosion Products

A. H. Roebuck, Continental Oil Co., Ponca City, Oklahoma, Chairman of Unit Committee T-3B on Identification of Corrosion Products has announced the completion of five bibliographies. They are: Corrosion Products of Titanium, of Stainless Steel, of Iron and Steel, of Zirconium and of Tin.

The committee anticipates that bibliographies on the following will be completed in the near future: magnesium,

TENTATIVE SCHEDULE
SOUTH CENTRAL REGIONAL MEETING

Houston, Texas, October 18, 19, 20, 21, 1955
Committee
T-1 Corrosion in Oil and Gas Well Equipment. All Day Tuesday
T-1C Sweet Oil Well Corrosion. 1:30 P.M. Wednesday
T-1D Sour Oil Well Corrosion. 8:30 A.M. Wednesday
T-1D-1 Fundamentals of Corrosion. 9:00 A.M. Thursday
T-1H Oil String Casing Corrosion, 10:00 A.M. Wednesday
T-1J Oil Field Structural Plastics. 9:00 A.M. Thursday
T-1K Inhibitors for Oil and Gas Wells. 1:30 P.M. Wednesday
T-2A-2 Ribbon Anodes. 9:00 A.M. Tuesday
T-2B Anodes for Impressed Currents. 1:30 P.M. Tuesday
T-2C Minimum Current Requirements for Cathodic Protection. 9:00 A.M. Wednesday
T-2D Standardization of Procedures for Measuring Pipe Coating Leakage Conductance. 1:30 P.M. Wednesday
T-2E Internal Corrosion of Product Pipe Lines and Tanks. 9:00 A.M. Wednesday
T-2J Wrappers for Underground Pipe Line Coating. 1:30 P.M. Tuesday
T-2K Prefabricated Plastic Film for Pipe Line Coating. 1:30 P.M. Wednesday
T-3B Identification of Corrosion Products. 1:30 P.M. Tuesday
T-4F-1 Water Meter Corrosion. 1:30 P.M. Tuesday
T-5B-2 Sulfide Corrosion at High Temperatures and Pressures in the Petroleum Industry. 9:30 A.M. Wednesday
T-5C-1 Corrosion by Cooling Waters, South Central Region. 1:30 P.M. Wednesday
T-6A Organic Coatings and Linings for Resistance to Chemical Corrosion. 9:00 A.M. Tuesday
T-6B Protective Coatings for Resistance to Atmospheric Corrosion. 9:00 A.M. Wednesday
T-6E Protective Coatings in Petroleum Production. 9:00 A.M. Thursday

aluminum, chromium, nickel, copper, zinc, silver, lead and molybdenum. When all bibliographies are complete they will be compiled and published as a report of the committee.

Directory of Committees Included in Yearbook

A directory of technical committees is included in the 1955 NACE Yearbook which was mailed to all members of the association in July. Included in the committee directory are the names, designations, scopes, officers and personnel of each committee.

Any NACE member not now active but who would like to join one or more committees is invited to study their scopes and communicate with the chairmen of those in which he is interested.

Corrosion magazine's abstract section includes over 1400 abstracts a year.

•

Five Technical Committee reports have been published in 1955 by NACE through June.

Reforming Units to Be Considered First In Investigations

Task Group T-5B-2 on Sulfide Corrosion at High Temperatures and Pressures in the Petroleum Industry, held an organizational meeting in the Jefferson Hotel in St. Louis, Missouri May 9. Twelve members and guests attended the meeting. M. E. Holmberg, Consulting Metallurgist, Houston, Texas, acted as temporary chairman of the meeting and was subsequently chosen permanent chairman.

The task group originated during the NACE Eleventh Annual Conference in Chicago last March. The problem of sulfide corrosion at high temperatures was included on the agenda of the T-5B meeting on high temperature corrosion and when it became evident at the T-5B meeting that many persons in the refining industry were concerned about the problem and the task group was assigned its study.

Information Exchange Planned

Chief function of the group will be to provide a means for persons interested in sulfide corrosion at high temperatures to exchange information. While the title, "Sulfide Corrosion at High Temperatures and Pressures in the Petroleum Industry" indicates interest is limited to refining operations, the task group recognized that other industries and organizations may wish to cooperate in a study of the problem. Process designers, construction companies, the steel industry, chemical companies, schools and other organizations, who might contribute to the work of the group are invited.

In defining the problem, the group said the refining industry has had experience with sulfide corrosion for many years. This resulted in the development of a 4-6% chromium-molybdenum steel for still tubes and other high temperature services. This alloy and other chrome-moly steels developed later, proved to be economical solutions to most of the high temperature sulfide corrosion problems encountered in refining service. But many new reforming units have been built in recent years and in 1954 severe corrosion was found in some of these units. The corrosion was in equipment in contact with gas containing hydrogen sulfide at high temperatures. In contrast with past refinery experience, the chrome-moly steels were often attacked as severely as carbon steels. It was evident a new corrosion problem had developed.

Reforming Units First

The problem is serious, not only because of metal loss, but also because a thick, brittle, corrosion product develops that breaks loose and plugs equipment. This is so serious that Task Group T-5B-2

High Temperature —

(Continued From Page 67)

has decided it will limit its work to sulfide corrosion at high temperatures in reforming units. However, it will draw on experience in other operations and processes.

A summary of the factors considered include:

Corrosion has been experienced in the temperature range 500-1200 F. As further information is developed, it may be necessary to extend this range, but for the present, the problem will be considered as one within the above stated temperature range.

The problem has developed in equipment operating above 200 psi.

The effect of pressure has not been established definitely, especially with respect to partial pressures.

There is evidence that the corrosion occurs at hydrogen sulfide concentrations as low as .005 percent by volume.

The corrosion has been experienced in concentrations up to 2 percent hydrogen sulfide by volume.

There is some correlation between concentration and rate of corrosion, but this is not in direct proportion over the entire range.

Some of the most severe corrosion has occurred in streams high in hydrogen. There is a definite possibility that the hydrogen affects the films that are normally

protective to the chrome-moly steels and that reducing conditions might result in the formation of a very corrosive phase in contact with the metal. The effect of hydrogen and its importance has not yet been established.

The effects of water and oxygen are being considered by some investigators. Its importance has not yet been definitely established.

There have been reports indicating that chlorinated solvents, lead, bromine, ethyl compounds, chlorides and other "stray" materials and associated factors may be influencing the corrosion.

The problem is being considered as a reforming problem, but it also may prove to exist in other operations involving sulfides at high temperature.

May Not Be Recognized

Indications are that the problem exists in many reforming units but has not yet been recognized because the units have been on stream for only a short time and have not yet been shut down for inspection. This proved to be the case in at least one refinery.

One phase of the problem might be to determine why this type of corrosion has not been serious previously in refineries.

Pressure vessels, heat exchangers, piping, valves, heating tubes and other equipment in contact with the hot gases have been corroded. As indicated above, the chrome-moly steels have not been effective, especially those containing 5 per-

cent chrome and less. Even the austenitic steels are corroded. Aluminum coated steel shows some promise but has disadvantages and limitations. Refractory coatings may not prevent attack.

New Probe Evaluated

At the organizational meeting it was revealed that one company is experimenting with a "Corosometer Probe" being developed by a research company. Information concerning experience with the probe will be furnished T-5B-2 when tests now underway are completed. Another company is operating a pilot plant in which materials are being exposed. These include different types of coating. Inhibitors were discussed. Most of the inhibitors checked to date have not been effective at the elevated temperature but one company reported preliminary tests have indicated one inhibitor might have application up to 650 F.

Next meeting of the task group will be during the NACE South Central Region meeting at the Shamrock-Hilton, Houston, Texas, October 18-21, 1955. NACE members interested in becoming active in the work of the committee are invited to the meeting.

•

Bibliographic Surveys of Corrosion published by the NACE contain abstracts carefully indexed and cross-indexed according to the NACE's Abstract Filing System.

Numerous Solutions to Oil Well Corrosion Problems Are Reported to Committee T-1F

Rod failures ceased for 15 months in a test well in Oklahoma after the well's pumping cycle was decreased only a few strokes per minute to comply with proration limitation. This was reported to Unit Committee T-1F on Metallurgy by a member of the committee.

Another member of the committee has reported on a mixed tubing string tested in a Western Kansas disposal well. The string was in service in an environment of brine containing hydrogen sulfide, carbon dioxide and a minimum of air. The string consisted of galvanized wrought iron Dimetcoted H-40 (later replaced with galvanized H-40) 9 nickel, 9 chrome and 5 nickel. When after 17 months no actual failure had occurred the string was pulled and all joints examined immediately. A dialog survey was run and some joints were cut open their full length for visual examination and measurement of pitting.

Pitting Factor Weighed

To arrive at a workable pitting factor, the ten deepest pits in each joint were measured and averaged. Results from the two methods of measurement were considerably at variance. Based on the visual test the member said his company plans to use galvanized wrought iron in disposal wells. Other members of the committee did not agree with the choice because of their own experiences.

In a discussion of steel nickel plated by the Kanigen process it was developed that the high phosphorus content of the Kanigen plating reduces its ductility as compared with electro-plated nickel. This reduces its resistance to brittle cracking which exposes the steel beneath.

Nickel Alloy Tubing Cracks

It has been reported to the committee that 9 percent nickel tubing in condensate wells has been experiencing stress corrosion cracking. The cracks are characteristically brached, transgranular and in the longitudinal direction. Pressure stresses appear to be the major factor. The cracks are extremely fine and cannot be detected with powder Magnaflux. Magnaglo shows them readily.

The committee has discussed the possible value of copper bearing steels for marine well structures, but their general use was not recommended. Corrosion resistance of such materials is dependent upon initial formation under alternately wet and dry conditions of a protective film. In many installations the steel is wet a greater part of the time; therefore, the rust would not be protective in these instances.

As a new project, the committee has decided to collect, correlate and disseminate data as it becomes available on high-strength tubular material, its composition, mechanical and physical properties and its performance with regard to corrosion behavior in sweet oil environments. This decision was made following a discussion by the committee on specifications for high-strength tubular goods for use in high-pressure sweet wells.

Roebuck Is Named Vice-Chairman of T-3

Dr. A. H. Roebuck, Continental Oil Co., Ponca City, Oklahoma, has been elected vice-chairman of NACE Technical Group Committee T-3 on General Corrosion Problems.

Dr. Roebuck received his master's degree from the University of Arizona and his PhD from the University of Texas. Before joining the research staff of Continental Oil Co., he was doing corrosion research work with the Reactor Engineering Division of Argonne National Laboratories where he engaged in the study of the corrosion of stainless steel, zirconium and other metals at elevated temperatures.

Roebuck

He has been a member of NACE since March, 1954 and in this short time he presented a paper at a national conference, becoming a leader of Unit Committee T-3B on Identification of Corrosion Products and will be the chairman of the High Purity Water Symposium at the 1956 NACE Conference in New York.

Dr. Roebuck will serve as vice-chairman of Group Committee T-3 until the last day of the NACE Conference in 1957.

●

The Bibliographic Survey of Corrosion for the years 1950-51 includes 4154 abstracts of literature topically indexed and cross-indexed.

Some Problems Allied to Sour Oil Well Corrosion Considered by Group

The West Texas-New Mexico task group of Unit Committee T-1D on Sour Oil Well Corrosion has reported on the use of inhibitors in sour oil wells and corrosion problems associated with water flood projects which use sour water. One member reported a reduction in rod breaks in one well from 12 to 3 per month by use of a commercially available inhibitor. Another member reported the failure of a plow steel line exposed in a well for 16 hours in a bottom hole instrument test in a West Texas field. The line had been coated with a grease type corrosion inhibitor.

Another member gave a preliminary report on a case of severe corrosion in a water flood project. A bare steel line carrying about 1000 barrels of water per day failed a few weeks after installation. The water, which was sour, gave a coupon corrosion rate of 0.040-inch per year on a laboratory weight loss test. The member is now testing a one coat catalyzed Epon system.

Another member reported a similar case of severe corrosion a bare discharge line in a water flood project. A plastic liner of 50 mils thickness was pulled through the pipe. This remedy appears to be satisfactory. One member reported that the use of submerged combustion for removing hydrogen sulfide from sour flood water appears to be giving satisfactory results. One member reported on plans for putting a cement lining in pipe made of 10 gauge steel for use in a water flood project.

Meetings held by the Kansas and West Texas-New Mexico task groups of T-1D emphasize the lack of information on certain aspects of corrosion in sour oil wells. For example the Kansas group could not agree on the volume of well fluids which should be used to flush an inhibitor into the well. This and other questions will be answered in the committee's next interim report.

New T-3 Chairman Has Studied Corrosion More Than Seventeen Years

Frederick W. Fink was appointed chairman of NACE Technical Group Committee T-3 on General Corrosion Problems at the expiration of F. M. Watkins' term of office in March of this year. Mr. Fink currently is Assistant Chief of the Corrosion Technology Division of Battelle Memorial Institute, Columbus, Ohio. He has been on Battelle's staff since 1938 where he has specialized in corrosion studies. Much of his work has been with the nonferrous metals and stainless steels.

He has been active in the Gordon Conference on Corrosion of the American Association for the Advancement of Science, serving on various occasions as discussion leader and, in 1951, as chairman. In 1952-1953, he was chairman of the Corrosion Division of the Electrochemical Society.

Mr. Fink's studies have resulted in publications covering such diverse corrosion problems as the attack of magnesium by marine environment, fretting corrosion, metallic corrosion by flue gas condensates and corrosion in oil-well equipment. Some of the corrosion work he is associated with has involved field work in such places as Alaska, Northern Canada and Florida.

He is active in the National Association of Corrosion Engineers, the Electrochemical Society and the American Institute of Mining and Metallurgical Engineers.

After obtaining his engineering degree at Cornell University, he devoted two years of graduate study in Germany and England (1935-1937). His M.Science from the University of Cambridge (England) was based upon a condenser tube corrosion problem.

Fink

Water Meter Corrosion Dircussion Scheduled

R. W. Henke, Badger Meter Manufacturing Co., Milwaukee, Wisconsin has announced that Task Group T-4F-1 on Water Meter Corrosion will hold a meeting during the NACE South Central Region meeting in Houston, October 18-21, 1955.

Mr. Henke has outlined a course of action for the committee's work which should result in an accumulation of data sufficient to permit learning much about the water meter corrosion and how to combat it. NACE members interested in this vital problem are invited to attend the meeting in October when Mr. Henke will accept applications for committee membership. He may be reached by mail at: R. W. Henke, Badger Meter Manufacturing Co., 2371 North 30th Street, Milwaukee 45, Wisconsin.

Bibliographic Surveys of Corrosion published by the NACE contain abstracts carefully indexed and cross-indexed according to the NACE's Abstract Filing System.

Four Problems Assigned To New HF Study Groups

T. L. Hoffman, Phillips Petroleum Co., Idaho Falls, chairman of T-5A-6 on HF Corrosion Problems has announced the assignment of project groups to study four specific problems.

Robert R. Pierce, Pennsylvania Salt Manufacturing Company, is leading the "HF" manufacturing group. This group proposes to investigate corrosion problems existing in kilns at 600 F, coke scrubbers, neutralization systems, purification product handling materials, safety devices, gaskets used in the process and protecting areas adjacent to the manufacturing installation from atmospheric contamination.

H. H. Bennett, Socony Mobil Oil Company is chairman of the group assigned to study cracking tower corrosion. This group will study blistering of steel, fume scrubbing systems, weak acids formed during operational fluctuations and protection of areas adjacent to the alkalate cracking tower installations.

H. O. Teeple, The International Nickel Co., Inc., heads the group assigned to study corrosion problems in the production of agriculture fertilizer grade phosphates. Using "HF" in producing agriculture fertilizer grade phosphates presents at least five known corrosion problems. These are: hydrofluoric acid digestors, stripping hydrofluoric acid from the process streams at 1400-1800 F, phosphorous pentoxide absorption towers, formation of hydrofluoric acid and safeguarding areas adjacent to the production facilities.

N. D. Groves, General Electric Company, is chairman of the group assigned to study the corrosion of hydrofluoric acid solutions in the process industries. Corrosion mitigation of solutions containing hydrofluoric acid for pickling stainless steels, Atomic Energy Commission unclassified uses of HF in the recovery of uranium from ore and reactor grade fuels are proposed work for this group.

Symposia at Regional Meeting Are Sponsored By Technical Committees

Group Committee T-1 is sponsoring the Symposium on Oil and Gas Production and Unit Committee T-1M is sponsoring the Marine Corrosion Symposium during the South Central Region meeting at Houston, October 18-21.

W. F. Oxford, Jr., Sun Oil Company, Beaumont, Texas and Jack L. Battle, Humble Oil & Refining Company, Houston, chairman and vice-chairman respectively of Group Committee T-1, will serve as chairman and vice-chairman of the symposium. D. F. Dial, Jr., The Pure Oil Company, Houston, chairman of T-1M, will serve as chairman of the Marine Corrosion Symposium.

Group Committee T-2 on Pipe Line Corrosion is sponsoring Pipe Line Group Discussions to be held during the meeting.

T-5C-1 on Corrosion by Cooling Waters, South Central Region, will contribute to the Symposium on Recirculated Water. This symposium will be held in two sessions each of one half day duration.

Unit Committee T-5B on High Temperature Corrosion will contribute to the Symposium on High Temperature. One paper presented will be of special interest to the new task group T-5B-2 on Hydrogen Sulfide Corrosion at High Temperatures and Pressures in the Petroleum Industry.

A schedule of technical committee meetings is published elsewhere in this section of CORROSION. All committee members are urged to be present at meetings and to attend the technical program.

Zimmerman Is Elected Vice-Chairman of T-5

R. I. Zimmerer, Westvaco Chlor-Alkali Division of the Food Machinery Chemical Corp., South Charleston, West Virginia, has been elected vice-chairman of NACE Technical Group Committee T-5 on Corrosion Problems in the Process Industries.

Mr. Zimmerer has been active in NACE activities since 1949. He is a charter member of the Kanawha Valley Section of the association and was one of the members instrumental in its formation. He has been chairman of Technical Unit Committee T-5A on Corrosion in the Chemical Manufacturing Industry and of the Task Group T-5A-4 on Chlorine since they were formed.

Mr. Zimmerer will serve as vice-chairman of Group Committee T-5 until the last day of the NACE Annual Conference in 1957.

●

For the seven years 1945-51 inclusive covered in the NACE Bibliographic Surveys of Corrosion there are 12,414 abstracts of technical literature on Corrosion. Most of these include a complete reference to original publication.

Schematic drawing of pioneer Swenson Evaporator shown in photograph. Operators say continuous finishing is easy to control automatically and uses only ½ as much fuel as batch finishing.

The information on the continuous caustic finishing unit is published through the courtesy of the Swenson Evaporator Company and Dr. W. L. Badger, originator of the process and designer of the unit.
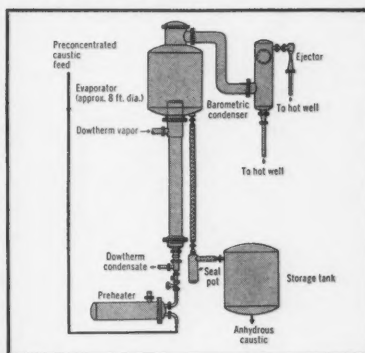
Schematic drawing of present simplified Swenson Evaporators. In these later units, jacketing is eliminated; thermal insulation prevents freeze-up. Low-carbon nickel tubes, tube sheets, shells and piping keep corrosion low and prevent product contamination.

Nine years commercial experience in the continuous finishing of anhydrous caustic soda in this pioneer Swenson Evaporator shows • • •

You don't have to "shade" solid NaOH made in nickel

What's more . . .

- With good control of chlorate, metal pick-up does not exceed 1 or 2 parts per million.

- Original equipment costs only 1/5 as much as a batch-finishing, direct-fired, iron pot installation of equal capacity.

- A set of nickel tubes can finish some 17,000 tons of caustic and costs less than 1/2 as much to replace as pots.

Modern practice is to produce 99.5% solid NaOH continuously in Dowtherm*heated evaporators with contact surfaces of corrosion-resistant nickel. Feed is either 50 or 73% NaOH from which chlorates have been removed by chemical reduction.

"Shading" pots originally installed with the Swenson Evaporator shown, have never been needed. In later installations, caustic is packed directly from the nickel storage tanks without "shading" or final purification.

THE INTERNATIONAL NICKEL COMPANY, INC.
67 Wall Street   New York 5, N. Y.

For further information on continuous caustic finishing units, write Swenson Evaporator Company, Harvey, Illinois. For assistance with caustic corrosion problems, contact Inco's Corrosion Engineering Section.

*Trademark of the Dow Chemical Company

INCO Nickel Alloys

NACE News

Houston October Meeting Program Is Outlined

1956 CONFERENCE LOCAL ARRANGEMENTS COMMITTEE is shown at its first meeting. Left to right members present are: E. G. Brink, American Viscose Corp., chairman conference coordination; Mrs. B. J. Bailey, Consolidated Edison Co., chairman ladies' activities committee; Herbert O. Teeple, The International Nickle Co., Inc., chairman printing committee; Carl R. Johnson, The Port of New York Authority, chairman publicity committee; Frank Miller, Hills-McCanna Co., chairman entertainment and hospitality committee; F. J. LeFebvre, Electro Rust-Proofing Corp., co-chairman local arrangements committee; Kemptom H. Roll, Lead Industries Assoc., general conference chairman; F. E. Kulman, Consolidated Edison Co., co-chairman local arrangements committee; Nelson N. Ehinger, Aluminum Company of America, chairman hotel and meeting rooms committee; M. Bermann, Brooklyn Union Gas Company, chairman transportation committee; J. G. Fitzpatrick, Hills-McCanna Co., hospitality and entertainment committee; Alton F. Minor, American Telephone and Telegraph Co., chairman registration and information committee. Not present for the meeting were Wayne Z. Friend, The International Nickel Co., Inc., chairman technical program committee, and C. A. Bailey, Johns-Manville Co., chairman exhibits committee.

Firms Contribute to Success of Program

Names of the firms contributing to the sustaining fund for the October 18-21 meeting of the South Central Region NACE at the Shamrock-Hilton Hotel are as follows:

Alco, American Locomotive Co.; Alcoa, Aluminum Co. of America; Allen Cathodic Protection Co., Inc.; Amercoat Corporation; Aquaness Corporation; Brance-Krachy Co.; A. M. Byers Co.; Cameron Iron Works; Cardinal Chemical Co.

Cathodic Protection Service; Coast Paint & Lacquer Co., Inc.; Corrosion Rectifying Co.; Corrosion Services Inc.; Crane Co.; Crutcher-Rolfs-Cummings, Inc.; Dow Chemical Co.; Dowell, Inc.; Odis C. Galloway & Co., Inc.

F. W. Gartner Co.; General Paint Corp.; Good-All Electric Mfg. Co.; Gulf States Asphalt Co.; Harbison-Fischer Mfg. Co.; Hercules Powder Co.; The Holcombe Co., Inc.; Huddleston Engineering Co.; Humble Oil & Refining Co.; Insul-Mastic Corp. of America; International Nickel Co., Inc.; Johns-Manville Sales Corp.; Koppers Co., Inc.; Magna of Texas; F. H. Maloney Co.; Mavor-Kelly Co.; Mayes Bros., Inc.;

Entertainment During Houston Meeting Set

A. L. Stegner, Tennessee Gas Transmission Co., Houston chairman of the entertainment committee for the South Central Region's 1955 meeting at the Shamrock-Hilton Hotel has planned the following events:

A pool-side cocktail party and buffet, Wednesday evening, October 19.

An anniversary dance party and floor show in the Emerald Room, Thursday evening, October 20.

A luncheon in the Shamrock Room, Friday, October 21.

Mr. and Mrs. T. F. P. Kelly are in charge of the ladies' entertainment program.

Technical Committees to Meet on Three Days

Technical committee meetings will be held all day Tuesday and Wednesday during the October 18-21 meeting of South Central Region at the Shamrock. Hilton Hotel, Houston. Four meetings will be held Thursday morning to complete 21 scheduled sessions.

Two Days of Session Completely Filled By 10 Symposia

An almost complete summary of the formal technical program to be given during the South Central Region's meeting in Houston October 18-21 has been released by Alvin E. Richie, Cathodic Protection Service, general chairman of the meeting. H. E. Morris, Monsanto Chemical Co., Texas City is technical program chairman.

The program is as follows:

Thursday, October 20—Morning

Pipe Line Industry Symposium, Charles L. Woody, United Gas Corp., Houston, chairman.

Basic Principles Involved in the Use and Interpretation of Reference Electrode Measurements by Maurice A. Riordan, Rio Engineering Co., Houston.

Cathodic Protection of Certain Semi-Marine Pipelines by B. J. Whitley, Tennessee Gas Transmission Co., Victoria, Texas.

Organizing Distribution Personnel for Cathodic Protection Installation and Maintenance by R. J. Uhr, United Gas Corp., New Braunfels, Texas.

Richie

Results of Coating Inspections on Cathodic Protection by J. A. Spracklen, Transcontinental Gas Pipeline Corp., Houston.

Chemical Processing Industries Symposium, W. G. Ashbaugh, Carbide and Carbon Chemicals Co., Texas City.

Corrosion Processing Acetic Acid and Related Compounds, E. V. Kunkel, Celanese Corp., Bishop, Texas.

Corrosion of Type 347 Stainless and Aluminum 1100 in Strong Nitric Acid and Mixed Nitric-Sulfuric Acids, C. P. Dillon, Carbide and Carbon Chemicals Co., Texas City.

Use of Stainless Steel Building Siding in Fertilizer Storage, G. R. Villemez, Olin Matheson Co., Pasadena, Texas.

Improved Laboratory and Field Method for Measuring Corrosion, Glenn A. Marsh and Edward Schaschl, Pure Oil Co., Crystal Lake, Ill.

Recirculated Cooling Water Symposium No. 1, M. C. Forbes, Aquatrol Inc., Houston, chairman.

Evaluation of Cooling Tower Corrosion Inhibitors by Charles B. Friedman

Firms Contribute—

(Continued From Page 77)

Midwestern Pipe Line Products Co.; The Natasco Co.

National Aluminate Corp.; National Tank Co.; Non-Corrosive Products Co.; Otis Pressure Control, Inc.; Parkerizing, Inc.; Tod Pazdral Pipeline Specialties; Perrault Equipment Co.; Philip Carey Manufacturing Co.; Pittsburgh Coke & Chemical Co.; Pipe Line Service Corporation; Plastic Applicators, Inc.; Plastic Engineering & Sales Corp.; Polyken Products.

Reilly Tar & Chemical Corp.; Rio Engineering Co.; E. W. Robinson Supply Co.; Rosson-Richards Co.; Sline Industrial Painters; Nowery J. Smith Co.; Socony Paint Products Co.; Standard Magnesium Corp.; The D. E. Stearns Co.; Thornhill-Craver Co.; Tret-O-Lite Co.; Tuboscope Co.; Tulsa Pipe Coating, Inc.; Visco Products Co.; WKM Manufacturing Co., Inc.; T. D. Williamson, Inc.

Houston Meeting—

(Continued From Page 77)

and W. L. Denman, Dearborn Chemical Company, Chicago.

Inhibiting Cooling Water Tower Systems by F. L. Whitney, Jr., Monsanto Chemical Co., St. Louis, Mo.

Four other papers are scheduled to be given in this symposium.

Thursday Afternoon
Recirculated Cooling Water Symposium No. 2.

Oil and Gas Industries Symposium, W.

Protective Coatings Round Table Panel—(Left to right), top, R. A. Brannon, Humble Pipe Line Co.; J. N. Hunter, Service Pipe Line Co.; middle, Loyd B. Nelson, Shell Pipeline Corp.; A. L. Stegner, Tennessee Gas Transmission Co.; bottom, Charles L. Woody, United Gas Corp., moderator.

F. Oxford, Jr., Sun Oil Co., Beaumont, Texas:

Iron-in-Oil Technique as a Corrosion Control Criterion, R. G. Rydell, Al Walker and Reed Robertson, National Aluminate Co., Chicago.

Report of Some Metallurgical Investigations for Materials to Control Corrosive High Pressure Wells, B. B. Morton, The International Nickel Co., Inc., New York.

Cathodic Protection of Oil Well Casings, G. L. Doremus, Cathodic Protection Service, Houston.

A Report on the Use of Alco Plating (Electroless Nickel Plating), Charles Paggi, Alco Products, Beaumont, Texas.

Protective Coatings Symposium, L. G. Sharpe, Napko Paint and Varnish Works, Houston, chairman:

Roundtable: Charles L. Woody, moderator; panel members, A. L. Stegner, Tennessee Gas Transmission Co., Houston; Russell A. Brannon, Humble Pipe Line Co., Houston; J. N. Hunter, Service Pipe Line Co., Tulsa, Okla., and Loyd B. Nelson, Shell Pipeline Corp., Houston.

Friday, October 21—Morning

Corrosion and Inhibitor Symposium, Norman Hackerman, University of Texas, Austin, chairman.

A Laboratory Method for the Evaluation of Oil Production Corrosion Inhibitors by David B. Boies, National Aluminate Corp., Chicago.

Corrosion Investigations Related to Adsorption Studies by C. C. Nathan, The Texas Co., Bellaire, Texas.

Sulfonates as Corrosion Inhibitors by A. H. Roebuck, P. L. Gant, O. L. Riggs and J. D. Sudbury, Continental Oil Co., Ponca City, Okla.

Control of Couples Developed in Water Systems by G. B. Hatch, Calgon, Inc., Pittsburgh, Pa.

Inhibiting Corrosion of Steel, Aluminum and Magnesium Intermittently Exposed to Brines by George E. Best and J. W. McGrew, Mutual Chemical Division, Allied Chemical and Dye Corp., Baltimore, Md.

Utilities Symposium, Charles M. Woodman, Southwestern Bell Telephone Co., Dallas, chairman:

Use of Copper Sulfate Half-Cells by Charlie Mercer, Southwestern Bell Telephone Co., Houston.

Corrosion Mitigation in Metropolitan Areas—Benefits from Cooperative Planning, Installation and Operation by M. C. Miller, Ebasco Services, Inc., New York, N. Y.

Telephone Cable Corrosion Problems by W. W. Elley, Southwestern Bell Telephone Co., San Antonio, Texas.

Marine Corrosion Symposium, P. F. Dial, Jr., The Pure Oil Co., Houston and O. L. Grosz, The California Co., Harvey, La., co-chairmen.

Cathodic Protection of Offshore Platforms, W. H. Edwards, Superior Oil Co., Houston.

Structural Design for Offshore Corrosion Control, D. B. Stauffer, Humble Oil and Refining Co., Houston.

Economic Considerations of Corrosion Control of Offshore Drilling and Producing Equipment, F. E. Blount, Magnolia Petroleum Co., Dallas.

Plastic Coated Magnesium Anodes, B. Douglas and C. F. Schrieber, The

---

ODESSA, TEXAS' downtown section. Lincoln Hotel, headquarters for the Sixth Biennial Corrosion Tour is at upper left. The Permian Basin radiates 200 miles about Odessa which is 2890 feet above sea level. October weather can be expected to provide warm, sunny days and chilly nights. The city, entertainment center for a wide area has many restaurants, night and

Elwell to Address Permian Basin Tour Session October 13; Program Is Revealed

Charles W. "Chuck" Elwell, vice-president of the administrative division, The Western Company, Midland, Texas will speak on "Corrosion Engineers or Corroded Engineers" during the Permian Basin Section's Sixth Biennial Corrosion Tour. His address will be on the night of October 13. Joseph E.

Elwell

Rench, Napko Paint and Varnish Co., Houston, will speak October 12 on the subject "What Paint Ain't."

The corrosion tour, scheduled to cover 60 exhibits in a 3000 square mile area, opens Wednesday, October 12. Hotel reservations are being made beginning October 11 because

of the early start needed on the morning of October 12. Nightly discussions of the day's tours will be held.

Space for exhibits in the main ballroom of the Lincoln Hotel in Odessa is available at $30. The fee includes a 6-foot table. Exhibits will be set up on the afternoon of October 11 and removed the afternoon of October 14.

A special request has been made of registrants by the exhibits chairman who asks visitors not to touch the exhibits and to keep all knives, files and electric sanders in pockets.

Registration fee of $20 includes air conditioned busses, barbecue, lunches and tour report booklet. Pre-registration may be made with E. O. Kemper, Permian Enterprises, Inc., Odessa, Texas.

Tentative Program

Thursday, October 11

1-5 pm—Registration.

Wednesday, October 12

7-8 am—Registration.
8-8:30 am—Welcoming address.
8:30 am-5 pm—Field Tour.
8-9:30 pm—Discussion of exhibits, followed by talk "What Paint Ain't" by Joseph E. Rench.

Thursday, October 13

8 am-5 pm—Field Tour.
8-9:30 pm—Discussion of exhibits, followed by talk "Corrosion Engineers or Corroded Engineers?" by Charles Elwell.

Friday, October 14

8 am-Noon—Field Tour.
Noon—Barbecue.

Water Treatment Talk Given Before 65 Persons

The August 8 meeting of Permian Basin Section was attended by approximately sixty-five members and guests. Gene McKenzie of Continental Products Company, Odessa, Texas, spoke on the subject "Fundamentals of Water Treating."

•

More than 1400 copies of Corrosion are mailed monthly to addresses outside the United States.

AT OAK RIDGE, TENN. meeting of NACE East Tennessee Section June 6, James L. English, section chairman, left; F. L. LaQue, speaker, middle and Wm. Manly, right.

Tests Simulating Service Conditions Recommended

The futility of trying to exactly correlate the results of accelerated corrosion tests with experience was underlined by F. L. LaQue, vice-president and manager of the Development and Research Division of The International Nickel Co., Inc. at a June 6 meeting of East Tennessee Section. Mr. LaQue's talk "Planning and Interpreting Corrosion Tests" was heard by about 40 members and guests at the meeting in Oak Ridge. William Manly, Oak Ridge National Laboratory, Metallurgy Division, was technical chairman.

Mr. LaQue stressed the importance of an all-out effort by the corrosion investigator to conduct corrosion tests under conditions which simulate as closely as possible the actual service environment for the metal or alloy being tested. He also touched on the effect of velocity on corrosion, the consequences of heat treatment and disadvantages of the commonly accepted salt spray test as a criterion for evaluation of coatings on metals.

Fall programs for the section include talks by E. C. Miller, Oak Ridge National Laboratory and W. A. Luce, The Duriron Company, Inc. A corrosion clinic to be held during the first two weeks in November will include discussions by selected speakers on problems related to pumps, valves, glass-lined equipment and general fabricated equipment.

Washington University Course Opens Sept. 12

A five-day Short Course on Corrosion will be given September 12-16 in St. Louis. The course, sponsored by University College and the School of Engineering, Washington University with cooperation of the National Association of Corrosion Engineers, covers a wide range of subjects by well-known lecturers.

Enrollment is limited to 100. Registrations made in advance must be accompanied by $10, applicable later to the $50 tuition fee. Reservations should be sent to University College, Room 102, Washington University, St. Louis, Mo. Housing is available at $2.50 daily in men's dormitories.

A complete program was published in CORROSION, June, 1955, Page 79.

1955-56 Chicago Section Program Is Outlined

A tentative program for the remainder of the 1955-56 year has been prepared by Chicago Section as follows:

Sept. 20—Ladies' night. Bakelite Corp. film "Flight Into the Future" will be shown.

Oct. 18—Burke Douglas, Dow Chemical Co. will speak on "Development of Galvomag Anodes and Their Uses."

Nov. 15—C. G. Munger, Amercoat Corp., will discuss "Good Structure Design Aids in the Battle Against Corrosion."

January 17—C. H. Samans, Standard Oil Res. Lab., will discuss "Corrosion Measurements."

Feb. 21—M. G. Fontana, Ohio State University, sponsored by The Duriron Co., will present a talk titled "Various Approaches to Corrosion Problems."

Mar. 20—D. C. Glass, Pure Oil Co.

will discuss "Survey of Pipeline Coating Practices and Protection Costs."

Apr. 17—E. F. Moorman, The International Harvester Co., will speak on "Economical Control of Corrosion Under Mildly Corrosive Conditions."

May 15—F. L. Whitney, Jr., Monsanto Chemical Co., will talk on "Use of Plastics to Solve Corrosion Problems in Industry."

The program committee consists of H. C. Boone, People's Gas Light and Coke Co., chairman; D. B. Sheldahl, Sinclair Research Laboratories, Harvey, Ill.; M. D. Fletcher, Illinois Bell Telephone Co., Chicago and R. E. Bowers, Industrial Coatings Corp., Chicago.

Shreveport Section Barbecue

Shreveport Section NACE will hold its annual barbecue September 20 in the American Legion Clubhouse, Shreveport.

Sand Blasting Extolled For Surface Preparation

Superiority of sand blasted surfaces for painting over power brushed areas was cited by James Cogshall, Pennsylvania Salt Mfg. Co., at a meeting of Detroit Section May 26. Eighteen members and 28 guests heard Mr. Cogshall say that a sandblasted surface provided a better bond for paint. Primers over brushed surfaces should be applied by brush for better adhesion, he recommended, while primers with special wetting agents and quick drying times are advantageous for areas exposed to chemicals.

While thinner materials rarely give more than 3 mils per three coat system, Neoprenes frequently give 2 mils per coat and satisfy better the requirements for a minimum of 5 mils for a satisfactory system, the speaker said. Principal saving is in labor when thicker films are obtained.

One speaker, during the discussion lead by Mr. Cogshall, maintained visual inspection on a 6 to 9-month schedule, with spot repairs saves from 40 to 50 percent over a system calling for new coatings every three years.

It was decided also that present section officers will have their terms extended to January 1956 to conform to the NACE standard terms of office.

Houston Meeting—

Dow Chemical Co., Midland, Mich.

Friday Afternoon

Cathodic Protection Symposium, Gordon Doremus, Cathodic Protection Service, Houston, chairman.

A High Potential Magnesium Anode, P. F. George, J. J. Newport and J. L. Nichols, The Dow Chemical Co., Midland, Mich., and Freeport, Texas.

Cathodic Protection Rectifiers: Some Factors to be Considered in Specifications and Design, Lyle R. Smith and Earl Newmyer, Good-All Electric Mfg. Co., Ogalalla, Neb.

Application of Cathodic Protection to Internal Tank Bottoms, J. W. Graves and O. R. Tisdale, Tidal Pipe Line Co., Houston.

High Temperature Corrosion Symposium, M. E. Holmberg, Consultant, Houston, chairman.

Liquid Metal Corrosion, W. D. Manly, Oak Ridge National Laboratories, Oak Ridge, Tenn.

Problems Encountered with Stainless Steel in Molten Lead Service at Elevated Temperature, W. R. Nisbet, Monsanto Chemical Co., Texas City.

High Temperature Hydrogen Sulfide Corrosion, R. D. Drew, C. C. Stapleford and E. B. Backensto, Socony-Vacuum Laboratories, Paulsboro, N.J.

Cathodic Protection Round Table Discussion, Derk Holsteyn, Shell Oil Co., moderator; panel members: Lionel Morrow, Interstate Oil Pipe Line Co., Shreveport, La.; L. P. Sudrabin, Electro Rust-Proofing Corp., Newark, N. J.; Scott Ewing, Carter Oil Co., Tulsa; Starr Thayer, consultant, Houston.

•

Bibliographic Surveys of Corrosion published by NACE contain abstracts carefully indexed and cross-indexed according to the NACE's Abstract Filing System.

Tough red Densheath (PVC) jacket.

Electrical-grade polyethylene insulation.

Your choice—copper or aluminum conductor. #8 through 750 Mcm.

Water Flood Corrosion Discussed at Houston

Ninety members and guests attended the August 9 meeting of the Houston Section in the Ben Milam Hotel to hear H. L. Bilhartz, president of Production Profits, Inc., speak on Corrosion in Water Flood. It was announced that future meetings of the section will be held at Captain John's Restaurant the second Tuesday of each month, with the exception of October. There will be no meeting in October due to the South Central Regional Meeting being held in Houston during that month.

W. B. Brooks of Dow Chemical Company, Freeport, will speak on Metals and Alloys in Sea Water at the September 13 meeting of the section.

Greater Boston Section Elects Officers for 1955-56

New officers for 1955-56 have been named as follows: Murray M. Jacobson, Watertown Arsenal Laboratories, Watertown, Mass., chairman; Edward C. Rue, Boston Edison Company, Boston, vice-chairman; Wayne H. Keller, National Research Corp., Cambridge, Mass., secretary.

South Central Board of Trustees Meets Oct. 19

A meeting of the South Central Region's board of trustees will be held at a luncheon October 19 during the 1955 regional meeting in Houston. The noon meeting will be at the Shamrock-Hilton Hotel at a room to be designated later.

Invitations to Exhibit At New York Sent Out

Invitations have been sent to prospective exhibitors at the 1956 Twelfth Conference and Exhibition of the National Association of Corrosion Engineers. The conference will be held March 12-16 at the Statler-Hilton Hotel, New York City. Clark A. Bailey, chairman of the 1956 Exhibits Committee said full details will be sent prospects later.

Loeffler Accepts Liaison Position on Publications

John E. Loeffler, Thornhill-Craver Company, Inc., Houston has agreed to act in liaison between the NACE Technical Practices Committee and the Publication Committee. He will resolve differences that arise in procedure and policy that occur in connection with the publication of technical material in CORROSION and elsewhere.

Effinger Named to Post On Program Committee

Robert T. Effinger, Shell Oil Co., New York City has been named co-chairman of the technical program committee for the NACE 12th Annual Conference and Exhibition. The meeting will be held at the Statler-Hilton Hotel, March 12-16, 1955.
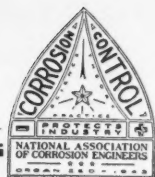
General News

AWS Corrosion-Related Papers to Be Given

Papers related to corrosion control scheduled to be given under the auspices of the American Welding Society during the 37th National Metal Congress and Exposition are as follows:

Effect of Preheating on Stress-Corrosion Cracking of Steel Weldments by E. Paul DeGarmo and I. Cornet, University of California.

Hot Cracking of Stainless Steel Weldments by P. P. Puzak and W. S. Pellini, Naval Research Laboratory.

Welding of Titanium by E. F. Gorman, Linde Air Products Co.

The Practical Approach to the Welding of Stainless Steel Pressure Vessels by Frederick H. Clash, Jr., Link-Belt Company.

Welding of High Temperature, High Pressure Piping With Chrome-Moly Electrodes by Lloyd C. Nesbitt, Metal and Thermit Corp.

PEI to Extend Porcelain Enamel Weathering Tests

The weathering test program started 15 years ago as a project of the Enameled Metals Section of the National Bureau of Standards will be expanded under sponsorship of the Porcelain Enamel Institute. The tests will be made by James H. Giles Jr., the PEI research associate at the bureau.

A newly formed Weathering Test Subcommittee of PEI with J. J. Canfield of Armco Steel Corp., as chairman will function as a subcommittee of the PEI Quality Development Committee.

Tests will be made on acid resistant types from AA to D and on numerous colors and types varying from full matte to full gloss. Specimens are mounted on rooftops in various locations and are compared from time to time with identical specimens stored in darkness.

Kroll Will Participate In NYU Titanium Program

William J. Kroll, inventor of the Kroll process for titanium extraction will be among 22 leading scientists and engineers scheduled to participate in a one-week program on titanium. The lectures are to be given at New York University's College of Engineering September 12-16. Evening discussion sessions will follow formal lectures.

Hot Dip Galvanizers

The American Hot Dip Galvanizers' Association, Inc., will hold its 1955 Semi-Annual Meeting September 29-30 at the Sheraton-Belvedere Hotel, Baltimore.

•

Corrosion is available on a subscription basis to non-members of NACE.

Coatings Intended for Marine, Offshore Duty Tested on Floating Rack in Corpus Christi Bay
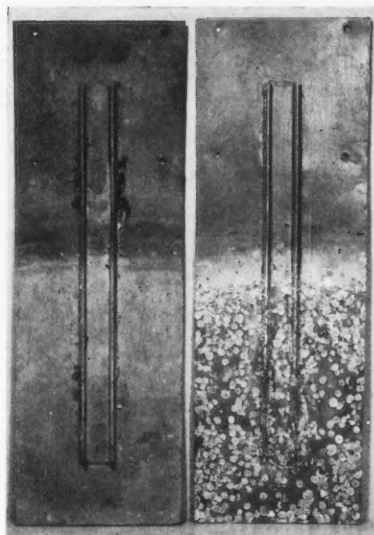
Figure 1—Comparison of results with two marine bottom paints after 8½ months' exposure in Corpus Christi, Texas Bay. Left panel is almost free of marine growth while right is liberally attacked by barnacles in submerged area. Both panels are in good condition in splash and ripple zone, with the only failures showing along weld seam of one panel.

Shop Practice Forum to Have Corrosion Papers

Papers to be presented during the Shop Practice Forum of the Porcelain Enamel Institute at Ohio State University, Columbus, September 14-16, include:

Fundamentals of Cathodic Protection by Forrest W. Nelson, A. O. Smith Corp.

High Temperature Coatings, D. G. Bennett, University of Illinois.

Electrical Conference

The National Electrical Conference of the Petroleum Industry, sponsored by the AIEE Petroleum Industry Committee and Houston Section AIEE will be held September 12-14 at the Shamrock-Hilton Hotel, Houston. Seven technical sessions and six field trips are scheduled.

•

For the seven years 1945-51 inclusive covered in the NACE Bibliographic Surveys of Corrosion there are 12,414 abstracts of technical literature on corrosion. Most of these include a complete reference to original publication.

Evaluation of coatings intended for use on marine and offshore exposures requires testing under the same conditions the coatings may be expected to encounter. The cover illustration on this month's issue of CORROSION shows one such testing rack. It is maintained in Corpus Christi Bay by Briner Paint and Mfg. Co., Inc., Corpus Christi, Texas for its own use and for the convenience of its customers.

The rack, which is in policed waters (through courtesy of a major oil company) provides a variety of exposures. The south-facing atmospheric racks are at 45 degrees. Other panels may be mounted at the edge of the rack as is the meter casing shown on the left. Another series is mounted on the outside edge of the raft where it is half submerged and half in the constant spray zone.

The 55-gallon drums on which the rack is mounted can be replaced without taking the raft from the water. Each drum is coated with a different bottom paint.

Any concern may apply for test data under the conditions provided by the raft. Although it has been in use only a year many requests for testing have been received.

The Briner company will prepare panels or other objects for exposure on request or will expose article sent to it. Data on the Briner technicians' examination will be given to interested parties and if desired Briner will make recommendations on improvements in the materials and methods used.

Submerged panels measure 8 x 24 inches and carry a 18-inch strip of ½ x 1½ inch channel welded to them. This gives shapes, edges and corners, weld seam and flat surface on one side. The other side is completely flat. Figure 1 shows comparison of two marine bottom paints after 18 months' exposure.

Arrangements can be made to include cathodic protection with or without coatings in submerged specimens. The company renders these services free of charge. John W. Nee, 3713 Agnes St., Corpus Christi, Texas has charge of the tests.

Electroplating Course

An eleven-week series of two hour sessions on basic practical electroplating will be held September 27-December 6. Meetings will be held at plating plants and laboratories in the Newark area with Dodd S. Carr, assistant director of Electrochemical Research, Bart Laboratories Co., Inc., Belleville, N. J. as chairman. Forty students have been accepted for the course.

•

An annual index to the abstracts published in the Corrosion Abstracts Section is published in December.

Inter Society Corrosion Committee

CORROSION MEETINGS
CALENDAR

1955
July 18-22—Gordon Research Conference, American Association for the Advancement of Science. Colby Junior College, New London, N. H.
Aug. 15-17—Society of Automotive Engineers, Inc. Golden Anniversary West Coast Meeting. Hotel Multnomah, Portland, Oregon.
Sept. 12-15—Society of Automotive Engineers, Inc. Golden Anniversary Tractor Meeting and Production Forum. Hotel Schroeder, Milwaukee, Wisconsin.
Sept. 15-16—Montreal Corrosion Symposium, Sheraton-Mount Royal Hotel, Montreal, Canada.
Sept. 25-28—American Institute of Chemical Engineers. Lake Placid, N. Y.
Oct. 3-7—American Institute of Electrical Engineers, Committee on Technical Operations. 1955 Fall Meeting, General. Morrison Hotel, Chicago, Illinois.
Oct. 9-13—Electrochemical Society, Inc. Fall Meeting. Pittsburgh, Penna.
Oct. 11-15—Society of Automotive Engineers, Inc. Golden Anniversary Aeronautic Meeting, Aircraft Production Forum, and Aircraft Engineering Display. Hotel Statler, Los Angeles, California.
Oct. 12-14—Sixth Biennial NACE Permian Basin Corrosion Tour.
Oct. 17-21—American Society for Metals. National Metal Congress and Exposition. Philadelphia, Penna.
Oct. 18-21—NACE South Central Region meeting, Shamrock-Hilton Hotel, Houston.
Oct. 31-Nov. 2—Society of Automotive Engineers, Inc. Golden Anniversary Transportation Meeting. The Chase, St. Louis, Missouri.
Oct. 31-Nov. 3—NACE Northeast Region meeting, Hotel Niagara, Niagara Falls, N. Y.
Nov. 2-4—Society of Automotive Engineers, Inc. Golden Anniversary Diesel Engine Meeting. The Chase, St. Louis, Missouri.
Nov. 9-10—Society of Automotive Engineers, Inc. Golden Anniversary Fuels and Lubricants Meeting. The Bellevue-Stratford Hotel, Philadelphia, Penna.

Nov. 17-18—NACE Western Region meeting, Sir. Francis Drake Hotel, San Francisco, Cal.
Nov. 27-30—American Institute of Chemical Engineers. Detroit, Michigan.
Nov. 27-30—American Society of Refrigerating Engineers. Annual Convention. Hotel Statler, New York, N. Y.

1956
Jan.—American Society of Heating and Ventilating Engineers. Annual Meeting. Cincinnati, Ohio.
Jan. 30-Feb. 3—American Institute of Electrical Engineers, Committee on Technical Operations. 1956 Winter Meeting, General. Hotel Statler, New York, N. Y.
Feb. 26-29—American Institute of Chemical Engineers. Los Angeles, California.
Feb. 27-March 2—American Society for Testing Materials. 1956 Committee Week. Statler Hotel, Buffalo, N. Y.
Mar. 12-16—NACE Twelfth Annual Conference and Exhibition, Statler Hotel, New York City.
May—American Institute of Chemical Engineers. Queen of Bermuda.
May 2-4—American Institute of Electrical Engineers, Committee on Technical Operations. North Eastern District Meeting. Rochester, N. Y.
May 7-10—American Gas Association. Distribution, Motor Vehicles, and Corrosion Conference. Congress Hotel, Chicago, Illinois.
May 10-11—American Gas Association. Gas Supply, Transmission, and Storage Conference. Conrad Hilton Hotel, Chicago, Illinois.
May 21-23—American Gas Association. Chemical, Engineering, and Manufactured Gas Production Conference. Hotel New Yorker, New York, N. Y.
June—American Society of Heating and Ventilating Engineers. Semi-annual Meeting. Washington, D. C.
June 17-22—American Society for Testing Materials. 1956 Annual Meeting. Chalfonte-Haddon Hall Hotel, Atlantic City, N. J.
June 25-29—American Institute of Electrical Engineers, Committee on Technical Operations. 1956 Summer and Pacific General Meeting. San Francisco, California.
Sept. 9-12—American Institute of Chemical Engineers. Pittsburgh, Penna.
Sept. 16-22—American Society for Testing Materials. 1956 Pacific Coast Meeting. Statler Hotel, Los Angeles, California.

Oct. 1-5—American Institute of Electrical Engineers, Committee on Technical Operations. 1956 Fall General Meeting. Morrison Hotel, Chicago, Illinois.
Oct. 2-5—NACE South Central Region meeting, Beaumont, Texas.
Oct. 28-Nov. 1—Electrochemical Society, Inc. Fall Meeting, Cleveland, Ohio.
Dec. 9-12—American Institute of Chemical Engineers. Boston, Massachusetts.

1957
Jan.—American Society of Heating and Ventilating Engineers. Annual Meeting. Chicago, Illinois.
Jan. 21-25—American Institute of Electrical Engineers, Committee on Technical Operations. 1957 Winter Meeting. Hotel Statler, New York, N. Y.
Feb. 4-8—American Society for Testing Materials. 1957 Committee Week. Benjamin Franklin Hotel, Philadelphia, Penna.
Mar. 11-15—NACE Thirteenth Annual Conference and Exhibition, Kiel Auditorium, St. Louis, Mo.
Spring (tentative)—American Institute of Electrical Engineers, Committee on Technical Operations. Northeastern District Meeting. Pittsfield, Massachusetts.

BOOK REVIEWS

About the Studies of Exposure Tests with Painted Steel Panels. A Report of Corrosion Commission IVa. (In Dutch) 36 pages, 5⅞ x 8⅜, paper. April, 1955. Mataalinstituut T.N.O. Afdeling Corrosie, Postbus 49, Delft, Holland, Per copy, 5 Francs.

This is the sixteenth report on this commission which started tests at five sites in 1935. Details of preparation of panels, coating systems, length of tests, nature of environment and other data are given. The information includes use of primers without finishing systems. These showed best results obtained with primers based on pigment mixtures containing at least 50 percent of red lead in raw linseed oil. Red iron oxide primers showed poor performance.

Tests with complete systems of primers and finishing coats involved various combinations of red lead primers, while lead finishing coats, asphaltic bitumen and water-resistant varnish. Numerous illustrations and tabulated data.

Combating Corrosion—A Special Symposium. A Digest of the Proceedings of the Corrosion Control Short Course, Extension Study Center, North Campus, University of Oklahoma, Tulsa. 184 pages, 8½ x 11, paper. April, 1955. Published by Business and Industrial Services, Extension Division, University of Oklahoma, Norman. Per copy, $2.

Consists of 26 papers given during the Corrosion Control Short Course, April 5-7, 1955 sponsored by the College of Engineering and Extension Division, The University of Oklahoma in cooperation with Central Oklahoma Section, National Association of Corrosion Engineers. Some of the papers are in brief abstract form only.

Titles and authors are as follows: Controlling Corrosion Thru NACE by John E. Loeffler; Theory of Inhibitors, A. H. Roebuck; Corrosion Inhibition and Bacteriological Control in Water Flooding, W. J. Ries; Application of Organic Inhibitors in Water Flooding, J. B. Robinson; Casing Corrosion in the Petroleum Industry, Jack L. Battle; Electrical Grounding in Cathodically Protected Systems, O. W. Everett; Corrosion Problems in Parallel and Cross-

NEW PRODUCTS — Materials — Service — Literature

Ferro-Pak, a volatile corrosion inhibitor impregnated paper made by the Cromwell Paper Co., 4801 S. Whipple St., Chicago 32, Ill. eliminates messy greasing and degreasing operations and still provides corrosion protection, the company says. Use of the paper cuts packaging and freight costs, and makes for a cleaner plant, according to the firm.

Hypalon, a new elastomer made by E. I. Du Pont de Nemours & Co., Wilmington, Dela., is described in the first issue of a periodical published by the company, "Facts About Hypalon." Chemically, the product is chlorosulfonated polyethylene. It is similar to rubber in appearance and physical characteristics, but is superior to rubber in many respects. Another Du Pont periodical publication, "Neoprene Notebook" features an instructive article, permeability of rubber. The article is part of a series on "The Language of Rubber."

Land Surface Pyrometer for accurately measuring high temperatures of metals and refractories when surrounded by cooler air is being marketed by Robertshaw-Fulton Controls. Fileden Instrument Div., 2920 N. Fourth St., Philadelphia 33, Pa. The measuring head of the instrument is mounted on a telescopic arm. When placed against a hot steel billet, the pyrometer will measure the temperature 3/16 inch below the surface within 0.5 percent accuracy.

American Hard Rubber Co. are manufacturers of a hard rubber pump for handling hydrofluoric acid in the production of television tubes. Each tube is washed three times in a high-velocity jet of 12 percent hydrofluoric acid. There is no metal-to-acid contact, the shaft is rubber covered as an integral unit with the impeller.

Compar, corrosion resistant hose and hose assemblies is described in a 4-page folder published by the Resistoflex Corp., Belleville 9, N. J., the manufacturers. The material, a modified polyvinyl alcohol resin compound, is entirely unaffected by all water insoluble liquids. Typical uses of the product and a list of materials it is especially suited for handling are given.

Isothane, a new two component polyurethane foaming resin has excellent dielectric properties, chemical resistance, thermal insulation and acoustical qualities, according to the maker, Surface Chemical, Inc., McKees Rocks, Pa. No steam lines, molds, heat or pressure of any kind are required to foam the plastic, the maker says.

Ladish Company, Kenosha, Wis., has designed a new industrial fitting for corrosion applications. The firm's "Tri-Clamp" fittings consist of a flange type ferrule—a special precision molded gasket which fits into the grooved ferrule lip—and the Tri-Clamp itself, which is composed of a specially fabricated spring clamp which grips the ferrule edges and a bolt-type coupler assembly firmly secured to the clamp ring.

Stainless tubular products used in steam superheaters, heater coils and oil refinery heaters and other high temperature applications are described in Technical Data Card 178 available from Tubular Products Div., The Babcock and Wilcox Co., Beaver Falls, Pa.

Stainless Steel Engineering Data, Catalog No. 55, giving information on flange drilling templates, ring joint facings, stainless steel pipe, pipe threads, pressure-temperature ratings, pressure-temperature relationship for saturated steam, hardness conversion tables and including a materials selection chart indicating the action of several hundred corrosives on several Cooper and other alloys is available on request. It is published by Cooper Alloy Corp., Hillside, N. J.

Pittsburgh Coke and Chemical Co. has added specialty tars, coal tar pitch and creosote to the products manufactured and sold by its protective coatings division. They formerly were handled by the company's coal chemicals division. N. T. Shideler, manager of the protective coatings division indicated the change will integrate the division's position with respect to coal tar coatings.

Fluoroflex-T Laminated pipe, of woven glass impregnated with Teflon is described in a 4-page bulletin issued by the Resistoflex Corp., Belleville, N. J.

Surface Roughness from one to 1000 microinches arithmetic average deviation from mean surface can be measured with the Brush Surfindicator, a portable instrument. Information can be obtained from Brush Electronics Co., 3405 Perkins Ave., Cleveland 14, Ohio.

Added Space will double the manufacturing and research area of American

BOOK REVIEWS

ing Systems, C. L. Mercer; Views of Management on Corrosion Control, Carl Cloud; Selling Corrosion Control to Management, J. C. Spalding, Jr.; Plastics for Pipe Coating, R. B. Bender; Sacrificial Anodes, P. F. George; Protecting Pipelines by Impressed Voltage, Scott Ewing; External Coatings for Pipelines, W. H. Stewart; Unwanted Currents on Pipelines, James R. Cowles; Prevention for Caustic Embrittlement in Boilers, James S. Connors; Corrosion Control in Steam and Condensate Systems, John J. Maguire; Corrosion Problems in Recirculating Cooling Tower Water Systems, R. S. Wise; Cathodic Protection in Refineries, V. W. Hatchett; "It's Up to You," T. L. Cannfield; Test Methods for Corrosion Mitigation, James R. Cowles; Microbiological Corrosion of Iron and Steel, D. M. Updegraff; Corrosion Problems in the Handling and Use of Sulfuric and Hydrochloric Acids, Harold E. Crook; Selection of the Proper Surface Coating for a Given Application, John W. Nee; Corrosion Resistance of Sprayed Metal Coatings, Walter B. Meyer; Use of Glass Coatings in Combating Corrosion, F. W. Nelson.

Agile Corp., 5461 Dunham Road, Maple Heights, Cleveland, Ohio.

A P-Type sink trap made of polyethylene is available from Arthur S. LaPine & Co., Chicago. It is similar to metal traps in construction and can be installed and dismantled by hand.

Impervite Heat Exchanger manufactured by Falls Industries, Inc., 31795 Aurora Rd., Solon, Ohio, is made of specially formed impervious graphite cubes housed in cast iron headers. A 15-inch cube provides 50 sq. in. effective heat transfer surface. The exchanger, normally made of Impervite, also can be fabricated of Graph-I-Tite, a new carbon-impregnated material capable of withstanding operating temperatures up to 5700 F. The cubical exchanger can be operated at pressures up to 100 psi.

Glass Cloth and fiber mat are impregnated with resins to form tanks for corrosive services varying in size from 6-inch cubes to 4 by 5 x 14-foot tanks. They are made by Valco Corp., 1710 Roblyn Ave., St. Paul 4, Minn., which also makes machine formed plastic tubing and pipe for use with the tanks.

Continuous Metallizing of plastic films and sheeting is possible in a new line of vacuum equipment available from F. J. Stokes Machine Co., 5500 Tabor Road, Philadelphia 20, Pa.

NEW PRODUCTS

(Continued From Page 88)

Knopp, Inc., is the new name for Electrical Facilities, Inc., Oakland, Cal., manufacturers of rectifiers and transformers and testing equipment.

New-Galv, a metal alloy stick useful in re-galvanizing areas where the zinc coating on steel has been damaged or destroyed by welding, flame-cutting, bending or the like is available from RotoMetals, 980 Harrison St., San Francisco 7, Cal. The stick metals and bonds at temperatures as low as 600 F and no flux or other treatment is required other than removing scale.

Corrosion-Erosion is the title of a small folder issued by Hall Laboratories, Inc., Pittsburgh, giving some of the economic reasons for corrosion control in boilers.

Aluminum Pipe roll-formed and welded from aluminum sheet in 2, 3 and 4-inch diameters is recommended by Kaiser Aluminum & Chemical Corp., Oakland, for fuel and water supply lines, salt water injection and disposal, low pressure flow lines and gathering systems in petroleum applications. A new quick connecting detachable coupling permits easy installation and recovery. The cast aluminum couplers engage the flared ends of the pipe with o-ring or moulded type Neoprene gaskets seated in coupler bodies by threaded locking nuts. The company claims 90-degree turns in four 30-foot lengths are possible without elbows or special connections.

Glass Fibers and thermosetting plastics are used to make cable clamps in size numbers 2 through 32 and cable diameters from ⅛-inch through 2-inch by Lunn Laminates, Inc., Huntington Station, N. Y. The small clamps are suggested for applications in the petrochemical, chemical, electric, electronic, marine and automotive fields where corrosion is a factor. The clamps materially lessen the danger of short circuits as compared to equivalent metal clamps.

Epon Curing agent BF 3-400, solid at room temperature, but easily stirred into warmed Epon 828 to yield catalyzed mixtures which remain useful up to several months stored at room temperatures has been developed by Shell Chemical Corp. Mixtures thus catalyzed and cured yield products with chemical and heat resistance superior to those of similar products cured with aliphatic polyamic curing agents. It is available in trial lot quantities.

Poly-Ep Platon, a finish which manufacturers, Minnesota Platon Corp., Pipestone, Minn., says can be applied directly to any clean metal surface without primer is now available. The finish may be applied by all conventional methods. The two-part material air dries dust free in 30 minutes and can be handled in 120 minutes.

Unplasticized Polyvinyl chloride now can be injection molded, by a process developed by Wilmington Plastics Co., 810 S. Heald St., Wilmington, Del. A custom-molding service is available from the firm.

Vidigage ultrasonic resonance thickness gages are described in a folder available from Branson Instruments, Inc., 430 Fairfield Ave., Stamford, Conn. The Vidigage directly measures the thickness of material from one side on a 21-inch television tube.

Deoxidizing Compound 89 is recommended by Enthone, Inc., New Haven, Conn., as a stripping material for all kinds of anodic coatings from aluminum. The alkaline material is used in aqueous solution at room temperature and does not include ingredients which make waste disposal a problem, manufacturers' claim.

Ultrasonic cleaners in 9-inch size soon will be added to other sizes manufactured by Pioneer-Central Division, Bendix Aviation Corp. The cleaners are being used in many industries to handle parts with intricate shapes and high precision surfaces which must not be altered by abrasion or etching.

Neoprene-Base protective covers to protect moving parts of machinery from dust and corrosives are manufactured by A. & A. Mfg. Co., Inc., 2017 Clybourn St., Milwaukee 3, Wis.

Tantalum-Lined steel heat exchangers fabricated by Merrem & LaPorte N. V., P. O. Box 59, Amsterdam C, Holland, are recommended for use with aggressive acids. Outside coatings may be as thick as 0.0116-inch and on the inner surface of the tube plate as thick as 0.020-inch. Linings are vacuum welded.

PERSONALS

M. D. Bellware has been named a member of the Welding Group of the Development and Research Division's Technical Service Section of the International Nickel Co., Inc.

O. A. Melvin, has been named sales engineer for the Texas and Louisiana Territory of The Carboline Co., St. Louis.

R. May, formerly Corrosion Advisor on condenser tube corrosion investigations at the Royal School of Mines has joined the Yorkshire Copper Works, Inc.

Russell L. Maycock has been appointed director of Shell Chemical Corporation's Houston research laboratory.

Raymond B. Seymour has been named president of Loven Chemical Company, Newhall, Cal. Dr. Seymour, who has published many papers on coatings and structural plastics formerly was president of Atlas Mineral Products Co. He is a member of NACE.

Frederick L. Feldmeth has accepted a position as sales engineer with the National Alloy Division of Blaw-Knox Company, Pittsburgh.

George William Lucas, 46, supervisor of carbide materials and process engineering, Carboloy Dept., General Electric Co., Detroit, died suddenly July 28. He joined the Carboloy organization 27 years ago.

Carl B. Post, head of Carpenter Steel Co., Metallurgical and Research Departments has been promoted to vice-president in charge of metallurgy.

Peter W. Schipper, general manager of the Investment Casting Div., Howard Foundry, Milwaukee has been named a director of the Investment Casting Institute.

Raymond E. McGrath has been named manager and **Vincent J. Hall** assistant manager of the combined Chicago plant and sales office of Reilly Tar & Chemical Corp.

Curtis B. Hoffman has been appointed vice president-sales of Brush Electronics Company, 3405 Perkins Ave., Cleveland 14, Ohio.

Lewis P. Favorite has been named manager of product sales; **Frederick J. Close** manager of market development and **W. S. McChesney** manager of Industry sales of Aluminum Company of America, Alcoa Bldg., Pittsburgh 19, Pa.

George Brown has been appointed manager of the Paulsboro, N. J. plant of Pennsylvania Salt Manufacturing Company's I. P. Thomas Division which produces commercial fertilizers, phosphoric and sulfuric acids and water conditioning chemicals.

Forest C. Monkman, Jr., a specialist in metals testing and research and a graduate of Massachusetts Institute of Technology has been named to head the new Research and Development Division of the Walworth Company at Boston. The new division will concentrate on development of valves and fittings for use in nuclear reactors.

Corrosion Abstracts

Index to
CORROSION ABSTRACTS

| Vol. 11 | September, 1955 | No. 9 |

2. TESTING

2.4 Instrumentation

2.4.3, 8.9.5

Corrosion Evaluation of Ship Bulkhead and Hull Plating by Audigage Thickness Measurements. Dwight J. Evans. *Corrosion*, 11, No. 3, 23-28 (1955) March.

Author discusses Audigage equipment under the divisions: theory of operation, characteristics and accuracy. Techniques for Audigage surveys of ship hull and bulkhead plating are given. Methods are particularly valuable in evaluating corrosion control systems now in use. Five figures, three tables, five references. Discussion. 8578

2.5 Specifications and Standardization

2.5, 2.3.4, 5.8.1

Proposed Standardized Laboratory Procedure for Screening Corrosion Inhibitors for Use in Oil and Gas Wells—A Report of Technical Unit Committee T-1K on Inhibitors for Oil and Gas Wells. J. C. Spalding, Jr. and E. C. Greco. *Corrosion*, 11, No. 3, 57-60 (1955) March.

The need for a standard laboratory procedure for screening corrosion inhibitors prior to field testing, for use in the oil and gas producing industry, was recognized by TP-1 (now T-1) in 1952. A paper presented at the 1953 NACE annual conference presented various methods of laboratory screening or evaluation being used. T-1K was organized for the purpose of developing a standardized test. As the result of the work of this committee, a standardized test has been devised and tested by various producing company laboratories. The test described in this report is a static oil and water immersion test using the weight loss of a steel coupon when under the influence of an inhibited system compared to its weight loss under an uninhibited system as a criteria of corrosion protection. 8739

5. PREVENTIVE MEASURES

5.4 Non-Metallic Coatings and Paints

5.4.1, 5.3.4

Corrosion Resistant Finishes. Arno J. Liebman. *Am. Paint J.*, 38, 26 + 6 pages (1954) Aug. 9.

Baked coatings; coatings in the form of linings; metallizing under organic coating systems; care along weld-seams; coatings in hidden areas. 21 references. —BTR. 8540

5.4.2

Role of Nickel Dip in Enameling of Sheet Steel. D. G. Moore, J. W. Pitts and W. N. Harrison. Paper before Am. Ceramic Soc., 55th Ann. Mtg., N. Y., April 29, 1953. *J. Am. Ceramic Soc.*, 37, No. 8, 363-369 (1954) August 1.

Investigation was made of the effects of firing time and weight of nickel deposited from nickel-dip solution on the adherence developed by a cobalt-free and a cobalt-bearing ground-coat enamel on both enameling iron and a titanium-stabilized low-carbon steel. Nickel-dip greatly improved adherence index for specimens fired a short time, but decreased adherence as firing time was in-

creased. Nickel-dip reduced tendency to fish-scale. No specimens with adherence index of 70 or over showed fish-scaling tendencies. Nickel dipping of the steel before enameling caused a surface roughening during firing operation; roughening is ascribed to galvanic corrosion. Tables, graphs, photomicrographs, 14 references.—INCO.   8627

5.4.5

Factors Influencing Premature Paint Peeling. *American Paint J.,* **38,** 66-87 (1954) January 11.

Discusses nature of problem with particular reference to overcoming paint peeling on southern yellow pine. Photographs, diagrams. 6 references.—BTR.
8572

5.4.5

Impermeable Organic Coatings. F. S. STEWART. *Orig. Finishing,* **15,** 8-10 (1954) May.

Mechanism of drying; indications of impermeability; and chemical resistance of certain single layer films. Graph, photographs.—BTR.   8746

5.4.5

The Mechanism of the Corrosion-Inhibitive Action of Paints, with Special Reference to Basic Pigments. J. E. O. MAYNE AND D. VAN ROOYDEN. *J. Applied Chem.* (London), **4,** No. 7, 384-394 (1954) July.

Lead and calcium soaps of linseed-oil fatty acids are shown to render water non-corrosive to iron and steel. Analysis of aqueous solutions of these soaps showed presence of salts of various organic acids: calcium and lead salts of azelaic, suberic and pelargonic acid were inhibitive at pH 4.6; calcium and lead formates were corrosive. Authors suggest two hypotheses to explain results.
—BNF.   8730

5.4.5

Coating with Mastics. R. B. SEYMOUR AND R. H. STEINER. Atlas Mineral Prods. Co. *Chem. Eng.,* **61,** No. 5, 232, 234, 236, 238, 240, 242 (1954) May.

Heavy coatings of properly applied asphaltic mastics protest steel structures and equipment against splash and fumes from salts, alkalis and non-oxidizing acids up to 150 F. Products of this type are not recommended for use in the presence of organic solvents, nitric acid, chromic acid, chlorine, sodium hypochlorite or chlorine dioxide. Corrosion test data are charted. Results were obtained from actual immersion tests even though asphaltic mastics are not normally recommended for this type of service.—INCO.   8636

5.4.5

New Acrylic Resins for Coatings. H. GRINSFELDER, W. C. PRENTISS, AND V. N. SHEETS. *Chemistry in Canada,* **6,** 29-33 (1954) Sept.

Advantages of new emulsion paints to consumer, painter, dealer, and manufacturer. Graphs, diagrams, photographs.—BTR.   8506

5.4.5, 2.2.5, 8.9.4

Why Pennsylvania Railroad Uses Aluminum Paint. *Railway Age,* **137,** No. 1, 30-31 (1954) July 5.

Between 1932-1937, several series of test paintings were made on catenary poles in the Schuylkill Valley from Philadelphia to Norristown, Pa., an area affording severe exposure conditions, using aluminum and grey oil as well as standard PRR black paint. In 1947 the test-painted installations were examined to determine general appearance, gloss, elasticity (or, conversely, brittleness), and amount of rust. The following factors were evaluated as a means of estimating remaining protection: spread of rust

spots, blisters, peeling and pitting. As a result of the tests, division engineers were instructed to apply aluminum paint when necessary to repair catenary and transmission poles. Later, the use of aluminum paint was extended to telegraph and signal apparatus over the entire system, and all structures where appearance was considered important including: undergrade and overhead bridges over important highways, catenary poles and bridges, transmission poles, signal and telegraph equipment, signal bridges, instrument houses and cases, unit compressor cases and air lines and telephone boxes and supports. On the basis of the earlier tests and periodic tests carried out since, the most suitable pigment and vehicles necessary to answer the railroad's maintenance needs have been determined.—ALL.   8681

5.4.5, 5.2.5

Zinc-Rich Compounds Give Cathodic Protection. H. L. GREBINAR. Galvicon Corp. *Steel,* **134,** No. 13, 113-114 (1954) March 29.

Iron and steel can be cathodically protected against corrosion by coating with vinyl resins heavily saturated with zinc powder. Coating, known as Galvicon (produced by Galvicon Corp.), which contains 96% zinc by weight when dry can be brushed, sprayed or dipped and affords protection against dilute acids and vapors, solutions of inorganic salts, humidity, sea and fresh water and salt atmospheres. J. E. O. Mayne coated steel plates with the zinc-rich compound, pierced them with a scratch line and placed them in sea water. They showed no evidence of loose rust after two years. Illustrations.—INCO.   8541

5.4.5, 6.3.19

Silicon Enamels: New Coatings for Zinc Base Die Castings. LYNN SPRAGUE. *Precision Metal Molding,* **12,** No. 9, 83-89 (1954) Sept.

Enamel is applied over a chemically inert surface layer, e.g., chromate or phosphate. Surface preparation, enamel application and baking, salvaging rejects, possible defects and how to overcome them.—BNF.   8712

5.4.7

Flame-Sprayed Plastic Coatings. M. M. RENFREW AND A. J. FREEMAN. *Org. Finishing,* **15,** 8-10 (1954) July.

Equipment and materials. Advantages and disadvantages. Photographs. 7 references.—BTR.   8736

5.4.8

Porcelain Enamel Fights Corrosion. W. A. BARROWS. Barrows Porcelain Enamel Co. *Power,* **98,** No. 7, 111-113, 220 (1954) July.

Examples of use of porcelain enamel to prevent corrosion in various situations, including temperatures up to 2000F, are coated black steel pipe in aluminum fluxing operation, conveyer screw for moving wet gypsum, glass-coated steel boiler tubing, porcelain enameled smoke-stacks, thermocouple protective tubes used in making aluminum, cast-iron deepwell-pump housing, heat-deflector cone of petroleum processing furnaces and catalyst contamination protection. Linings of chambers holding catalyst and material are now coated with porcelain enamel to prevent contact between nickel alloys and catalyst. Illustrations.—INCO.   8481

5.4.8, 4.3.3

New Epoxy Primer Has High Resist-

ance to **Alkalies.** H. L. FARBER. *Materials & Methods,* **39,** 93-95 (1954) Feb.

Advanced flow coating technique combined with new primer permits thinner film thickness and improves corrosion resistance three times. Photographs. — BTR. 8450

5.5 Oil and Grease Coatings

5.5.3
Investigation of Thin Coatings of Protective Greases for Preservation of Steel Objects. (In Russian). V. V. SKORCHEL-LETTI, A. I. BUKHBINDER AND V. E. PIS-KORSKII. *J. Applied Chem.* (Zhur. Priklad. Khim.), **27,** No. 4, 454-456 (1954) April.

Effectiveness of grease containing aluminum oleate. Tables. 1 ref.—BTR. 8654

5.5.3
Petroleum-Based Corrosion Preventives. R. LESLIE. *Corrosion Technology,* **1,** No. 7, 243-245 (1954) Sept.

Temporary corrosion preventives based on petroleum are applied to a variety of products ranging from ballbearings to sheet steel to give protection during manufacture, transport or storage. Main types of preventives, their selection for particular purposes, methods of application, types of and mode of action of inhibitors added to the preventives and methods of testing, are described. Six references.—INCO. 8520

5.8 Inhibitors and Passivators

5.8.1, 1.7.1
Some Corrosion Inhibitors—A Reference List—A Report of Technical Unit Committee T-3A on Corrosion Inhibitors. ROBERT W. WISE. *Corrosion,* **11,** No. 4, 65-67 (1955) April.

Chemical and trade names, sources of supply, utility classes in which useful, material with which effective and literature references for 68 inhibitors and classes of inhibitors are given. This list, consisting only of inhibitors for which literature references are available outside of manufacturers' literature, is conceded to be incomplete. Suggestions for additions and changes of presentation are solicited by the originating committee. 8611

5.8.2
Corrosion Inhibitor Checklist. M. BROOKE. *Chem. Eng.,* **61,** No. 12, 230, 232, 234 (1954) December.

Corrosion inhibitor checklist includes metals, environments, inhibitors and references. Admiralty, aluminum, brass, copper, iron, magnesium, Monel, nickel, stainless steel, steel and titanium are some of the materials covered.—INCO. 8568

5.8.2, 8.4.3
Use of High Molecular Weight Corrosion Inhibitors in Petroleum Refineries. H. HOWARD BENNETT. *Corrosion,* **11,** No. 2, 19-27 (1955) Feb.

The theory of adsorptive inhibitors is discussed briefly. An account is given of tests by coupons and in refinery equipment evaluating the effect of three semi-polar compounds in reducing the corrosion of refinery equipment. Data on concentrations, technique of additions to streams, coincident use of ammonia, cost per barrel of charge, percentages discharged in effluent and percentage retained in stream are given. Considerable information is revealed indicating the detergent action of the inhibitors assists in reducing deposits on tubes and in pumps

and other equipment and thereby extends the period between shutdowns for cleaning. Significant reductions in the corrosion rates in crude distillation units, steam reboilers, straight run deisobutanizers, vacuum pumps, alkylation units, TCC units and other refinery equipment are reported. The author concludes water soluble inhibitors tested are sufficiently soluble in hydrocarbons to provide corrosion protection. 8457

5.8.2, 8.4.3, 7.6.8
Use of Organic Inhibitors in Refinery Distillation Process Equipment. G. E. PURDY. *Corrosion,* **11,** No. 1, 64-67 (1955) January.

Use of a high molecular weight organic corrosion inhibitor is discussed. Recommended methods are given for use to inhibit losses from such corrosives as

hydrogen sulfide, hydrochloric acid, organic acids and salts. Secondary effects are explained, such as detergent effects, which make for less cleanup time for maintenance of designed heat transfer characteristics. Experiences in 120 refineries in the United States and Canada and 14 refineries in other countries are reviewed. 8458

5.8.3
Effect of Organic Molecules on the Adsorption of Hydrogen on the Electrode Surface. *J. Chem. Soc. Japan, Pure Chem. Sect.,* **74,** No. 10, 524-527 (1954).

An oscillographic study of the relation between electrode potential and adsorption of organic molecules showed two types of organic molecules: 1) Of dipole moment greater than that of water, strongly adsorbed, and causing the

cathode potential to become less noble. If the current density is corrected to the area covered, the potential reaches that of the solution without the organic compound. 2) Of dipole moment smaller than that of coatings and only weakly adsorbed. The effect on the potential here seems mainly due to solvent effect.—EL. 8500

5.8.3, 2.3.5
Inhibitor Evaluation by the Pearson Null Bridge. BARTON L. CROSS AND NORMAN HACKERMAN. *Corrosion,* 10, No. 11, 407-412 (1954) November.

A Pearson null bridge was built in order to determine its usefulness in the evaluation of corrosion inhibitors. Eight compounds and three commercial inhibitors were tested using steel in aqueous sodium sulfate solution as the corrosion system. The materials used all had been studied by various other means, thereby permitting comparison of previous results with those obtained by this method. As an estimate, this procedure gave about 70 percent correlation with other methods, as far as inhibiting mechanisms are concerned. This is on the basis of qualitative classification only. As a quantitative tool, the bridge in its present form appears to be considerably less useful. 8447

5.8.3, 5.8.4, 1.6
Corrosion Preventive Additives. E. J. SCHWOEGLER AND L. U. BERMAN. March, 1954, 166 pp. Armour Research Foundation, Contract AF 33(038)-9202.

The development of new corrosion inhibitors that may supplement or replace petroleum sulfonates was studied. The evaluation study was continued with major emphasis on the type of compounds which previously were shown to be effective inhibitors and the minimum effective concentration was determined. With certain amine salt inhibitors a study was made to determine the effect of heating at 150C for three hours on corrosion inhibition. A large number of organic compounds were screened by the use of a galvanic specimen test in order to discover inhibitors that might be effective for inhibiting corrosion in the bimetallic system, 52100 steel-Muntz metal brass. Conditions of temperature, humidity, etc., were studied to arrive at conditions best suited for screening these compounds. Initial studies were made on the mechanism of corrosion inhibition of 1020 steel. In the elucidation of the mechanism of corrosion inhibition, attempts were made to relate effectiveness to the structural and functional group characteristics of the molecules studied. The compound types studied included morpholine derivatives, aliphatic amines, and amine salts of various carboxylic acids in both AN-O-6a and MIL-L-6085A base oils. Many organic compounds were synthesized to assist in the development of new inhibitors and in the elucidation of the mechanism of corrosion inhibition. These included morpholine and ethylenediamine derivatives, amine salts of mono- and dicarboxylic acids, fatty acid derivatives and substituted glyoxalidines. An infra red study on 2- and 1,2-substituted glyoxalidines was made in an effort to arrive at an effective method of verifying these structures. This was essential since certain glyoxalidines were found to have potential inhibiting properties sufficient to warrant further investigation of this type of compound. (auth).—NSA. 8706

5.8.3, 6.2.2
The Mechanism of Inhibition of the Corrosion of Iron by Solutions of Sodium Phosphate, Borate and Carbonate. J. E. O. MAYNE AND J. W. MENTER. *J. Chem. Soc.,* 1954, 103-107, January.

Iron samples from which the air-formed oxide film had been removed were immersed in aerated 0.1 N Solutions of disodium hydrogen phosphate, trisodium phosphate, sodium borate and sodium carbonate. The films formed under these conditions were stripped by the alcoholic iodine method and their compositions were determined by electron diffraction and, when phosphate was present, by chemical analysis.

All stripped films showed large, continuous, homogeneous areas of even thickness consisting mainly of cubic oxide having the composition $Fe_3O_4 \cdot \gamma Fe_2O_3$ or an intermediate compound. In some regions there were denser particles about 1 μ or less in size. In the film formed in disodium hydrogen phosphate large particles of $FePO_4 \cdot 2H_2O$ were embedded in a matrix of cubic oxide. Trisodium phosphate yielded films containing only a small amount of ferric phosphate; with sodium carbonate and sodium borate, no clear evidence was obtained for the existence of a second phase.

Sodium carbonate, sodium borate and trisodium phosphate are the salts of weak acids, and their aqueous solutions are alkaline owing to hydrolysis; consequently the ferrous compounds formed at the anodes hydrolyze to ferrous hydroxide, which in alkaline solution oxidizes to an oxide having the cubic structure. In disodium hydrogen phosphate solution

(pH 8.4), however, the ferrous phosphate formed at the anodes is more stable to hydrolysis, but readily oxidizes to ferric phosphate.

Partial immersion in 1 N sodium tartrate solution containing disodium hydrogen phosphate indicated that the presence of phosphate in the film is necessary for inhibition when the air-formed film is thin, but not when it is thick. In films formed in tartrate solution containing trisodium phosphate only small quantities of phosphate were detected and these were not essential for the development of passivity.—PDA. 8618

5.8.3, 6.2.2, 6.2.3
The Mechanism of Inhibition of the Corrosion of Iron by Sodium Hydroxide Solution. Part II. J. E. O. MAYNE AND

J. W. MENTER. *J. Chem. Soc.*, **1954**, 99-103, January.

The anodic polarization of Swedish iron and annealed mild steel in 0.1 N sodium hydroxide was examined in the presence and in the absence of air. The film formed on the metal by the anodic discharge of hydroxyl ions showed the cubic structure of either Fe_2O_3 or $\gamma—Fe_2O_3$ and was indistinguishable by electron diffraction from the air-formed film. Except for traces of $\gamma—Fe_2O_3 \cdot H_2O$, the oxide was anhydrous and not hydrated as found by Russian workers in 2 N sodium hydroxide.

Freshly abraded iron became passive when immersed in 0.1 N sodium hydroxide containing dissolved oxygen. It is suggested that weak areas in the air-formed film are first repaired by the electrochemical formation of ferrous hy-

droxide, which then reacts with oxygen to form cubic Fe_3O_4, $\gamma—Fe_2O_3$, or an intermediate compound. Later repair, after a potential of —0.4 v. has been reached, may occur by the direct electrochemical production of ferric oxide. In this way, the film thickens until it becomes impervious to ions and passivity ensues. Thus, an air-formed film which may be months old can be rapidly reinforced by immersion in aerated 0.1 N sodium hydroxide, with or without the application of a current.—PDA. 8733

5.9 Surface Treatment

5.9.2, 5.9.3, 6.2.5
Descaling the Stainless Steels. L. F. SPENCER. *Metal Finishing*, **52**, No. 2, 54-59 (1954) February.

Difficulties in removing complex oxide scale from stainless steel; mechanical descaling; acid descaling; choice of acid pickling baths; caustic descaling baths. —BNF. 8382

5.9.2
Electrolytic Derusting: Principles and Applications of the Process. L. KENWORTHY AND T. F. EAST. *Engineering*, **178**, 235-237 (1954) August 20.

Process developed by the Admiralty for derusting iron or steel by cathodic treatment in sea water or sodium hydroxide (using 12 v. DC). Large articles such as buoys or mines can be treated when suspended in the sea and methods for treating large tanks and steam turbines are given. Decks are derusted by using a paste of sea water and asbestos fibre, or iron mesh electrodes in canvas bags of sea water.—BNF. 8545

5.9.2
Pickling in Acids—A Closed Cycle? Report No. 216 of the Committee of Chemists of the Verein Deutscher Eisenhüttenleute. (In German). WALTER FECKERT. *Stahl und Eisen*, **74**, No. 14, 888-894 (1954) July 1.

Chemical processes in pickling iron with sulfuric acid. Requirements to be met by a modern acid pickling method. Continuous pickling methods. Recovery of the spent acid by the application of novel theories. Testing in a pilot plant. The most appropriate conditions for the operation of the pilot plant. Laboratory tests for the disposal of the iron sulfate produced. Modification of the entire pickling process into a cyclic operation process.—SE. 8517

5.9.2
The Role of Cyanide Neutralization in the Surface Treatment of Steel. J. H. PETERSON, G. M. NICHOLS AND W. F. McDEVIT. *Metal Finishing*, **52**, No. 10, 62-64 (1954) October.

Carbon-14 was used to determine amounts of cyanide retained on pickled steel. Results show that improvement in temporary corrosion resistance of cyanide neutralized pickled steel stems entirely from chemical action of sodium cyanide during neutralization step itself. Tables. Two references. 8690

5.9.2
Chemical Polishing of Steel. W. A. MARSHALL. *Research*, **7**, No. 3, 89-93 (1954) March.

An account of the ARE smoothing process for steel, in which a bath containing oxalic acid, hydrogen peroxide and sulfuric acid is used. Although there are

some difficulties yet to be surmounted, this process appears to be suitable for preparing steel for electroplating—either decorative or for reclamation of worn components.—BNF.   8674

5.9.2, 5.8.2
Testing the Efficiency of Pickling Additions [Inhibitors]. (In German). H. HOFF AND G. VON DER DUNK. *Arch. Eisensuttenw.*, **25**, No. 3/4, 115-123 (1954) March/April.

Iron salts dissolved in the acid may increase attack on steel. The effect of numerous commercial inhibitors was studied; a few were found satisfactory in sulfuric acid at 90 degrees (for continuous pickling of strip). The presence of iron salts prolongs the pickling time, even when an effective inhibitor is present.—BNF.   8475

5.9.2, 8.9.5
Electrolytic Descaling—An Electrical Method of Rust Removal from Tanker Ship Compartments. F. E. COOK, H. S. PREISER AND J. F. MILLS. *Corrosion*, **11**, No. 4, 31-51 (1955) April; *J. Am. Soc. Naval Engrs.*, **68**, No. 4, 1005-1050 (1954) November.

A detailed report of the theory, technique and application of electrolytic derusting to the cargo tanks of United States Navy tankships. After a discussion of the various aspects of anodic and cathodic cleaning of rust from steels, the theory of the process together with an account of patents, army use of the method and initial navy testing and applications is reviewed.

Details of the laboratory investigations preceding the application of the descaling method are given, including apparatus and materials. Effects of anode

spacing, electrolyte composition, temperature, effect on faying surfaces and on dissimilar metals (aluminum, zinc, lead and brass), additions of sulfuric acid to electrolyte, current reversals, detergents, hydrogen embrittlement are surveyed. Results using anodes of magnesium, aluminum, zinc, copper and platinum are reported. Volume of gases given off by the various anodes is measured.

Reports on the electrolytic descaling of nine vessels are given including an estimate of the final tank conditions, optimum current density, anode area, current distribution, washing down operations, intermittent flushing, hydrogen evolution and cost comparisons with conventional cleaning methods. Specific recommendations and an account of the practical details involved in the procedure are given. 15 tables, 33 figures.   8621

5.9.3
Precision Barrel Finishing. M. M. MAYNES. *Plating*, 41, No. 1, 455-460 (1954) January.

Deburring and surface finishing: types of barrels, auxiliary equipment, media, cleaners, operating procedure and hints. —BNF.   8734

5.9.3
Belt Grinding or Wheel Grinding? Parts III, IV and V. (In German). G. PAHLITZSCH AND H. WINDISCH. *Metalloberflache;* Series A; 8; Nos. 6, 8, 9. A87-92, A119-125, A132-141 (1954) June, August, September.

Part III (June) deals with further ways and means of economic belt grinding; Part IV (August) with the use of mixtures of grease and petroleum and abrasives; and Part V (September) is a general economic comparison of ordinary grinding belts and abrasive-coated wheels

and includes the first results obtained on the recently developed multi-layer belt.—BNF. 8749

5.9.3
Polishing of Metal by the Barrelling Process. L. MABLE. Paper before Inst. Metal Finishing, Manchester, October 7, 1954. *Bull. Inst. Met. Finishing,* **4**, No. 4, 289-298 (1954-1955) Winter.

Practical methods for the barrel grinding and/or barrel burnishing of malleable cast iron, steel, brass and nickel silver parts and of zinc-base die-castings and for deburring and cleaning, are described. Design, layout, types of barrel, and suitable mediums are discussed.—INCO.
8580

•

The number of authors listed in the 1950-51 Bibliographic Survey of Corrosion published by the NACE is 4057.

5.9.4
Phosphating. R. F. DRYSDALE. Paper before Inst. Met. Finishing, Manchester, Feb. 18, 1954. *Bull. Inst. Met. Finishing,* **4**, No. 3, 203-218 (1954) Autumn.

A review of modern methods of phosphatation including a classification of the various types of coatings produced by present commercial phosphating methods by predominant metal phosphate in the treatment bath (iron, zinc, or manganese), weight per unit area of the coating, anti-corrosion and other purposes of the coating and accelerated and non-accelerated processes. Anti-corrosion uses of phosphate coatings are sub-divided into the protection of threaded components and/or moving parts, non-moving but rigid parts or structures, parts or components which are subject to flexure during service and parts which have to be formed or bent after treatment. Factors affecting the formation and crystal growth of phosphate coatings are briefly discussed. 11 references.—INCO.
8409

5.9.4
Effect of Gelatin on the Changes in Initial Cathode Polarization During Electrodeposition of Copper. B. I. PARSONS AND C. A. WINKLER. *Can. J. Chem.,* **32**, No. 6, 581-590 (1954) June.

In the absence of addition agent, the cathode polarization during initial electrolysis of copper from a solution of acid cupric sulfate rose almost instantaneously from zero to approximately the steady state polarization. When gelatin was present the polarization generally increased to a maximum; then decreased to a minimum beyond which it increased to a steady state value.—BNF. 8602

5.9.4
Some Hints on Good Phosphating Practices. H. A. HOLDEN, *Electroplating & Metal Finishing,* **7**, No. 11, 416-418 (1954) November.

Some defects and remedies of accelerated zinc phosphate treatment are tabulated. Five basic stages of phosphating comprise cleaning, phosphate coating formation, rinsing, drying, and after-treatment (staining, oiling, painting, lacquering and lubrication). These are outlined. Inadequate cleaning and contaminated rinses are the two main causes for complaint.—INCO. 8478

5.9.4
Aluminium: Hard Coating Methods Review. P. J. BRODEUR. *Light Metal Age,* **12**, No. 3/4, 10, 24 (1954) April.

Includes two tables on grit blast abrasion tests and salt spray corrosion tests on various anodic coatings, prepared by the Alumilite process of the Glenn L. Martin Co.'s "Martin Hard Coat" process.—BNF. 8516

5.9.4, 6.3.20
Analysis of the Formation Current in Electrolytic Oxidation of Zirconium. J. J. POLLING AND A. CHARLESBY. *Proc. Phys. Soc.,* (B), **67**, No. 3, 201-210 (1954) March.

In anodizing zirconium, only a portion of the current passed contributes to the growth of the insulating oxide film. The film thickness is proportional to the formation voltage and by measuring the mass increase of the specimen and correcting for trapped gases, the net weight-gain is found to be $0.41\gamma/cm.^2/V$. Values of the dielectric constant were also determined as $\mu 27$. The structure of the film is largely amorphous.—MA. 8693

6. MATERIALS OF CONSTRUCTION

6.2 Ferrous Metals and Alloys

6.2.5, 3.5.9
High Temperature Oxidation Characteristics of Some Manganese-Aluminium Steels. Part I. A. A. KRISHNAN AND VED PRAKASH. *J. Sci. Ind. Research* (India), **13**, Sec. B, 444-449 (1954) June.

Oxidation characteristics of some manganese-aluminum steels between 600 and 1100 C for short durations are reported. The manganese content of the steels varied from 0.4 to 26.2 percent and that of aluminum from 8 to 11 percent. The oxidation characteristics of most of the manganese-aluminum steels obey para-

bolic law at 600 to 700 C. The addition of manganese in 8 to 11 percent aluminum steels results in increased oxidation at all temperatures from 600 to 1000 C. However, steel containing 6.5 percent manganese and 8 percent aluminum resists oxidation slightly better than 11 percent aluminum steel at 1100 C. (auth).—NSA.
8543

6.2.5, 3.7.2

Rare Earths in Stainless Steels. H. O. BEAVER. Carpenter Steel Co. Paper before Am. Soc. Metals, Reg. Mtg., Penn State College. *Metal Progress*, **66**, No. 4, 115-119 (1954) October.

While rare-earth oxides and Mischmetall are useful degasifiers in complex and high-chromium-nickel austenitic steels, residuals from Mischmetall are necessary to correct brittleness at forging ranges. Improvements in hot workability is described. No effect of rare earths on corrosion resistance, tensile strength, impact properties or age hardening is noted. Stress-rupture is increased and scale formation to 1900 F is reduced, but above this temperature the scaling rate increases rapidly. Graphs.—INCO.   8485

6.2.5, 3.7.2, 3.2.2

Effect of Minor Constituents on the Intergranular Corrosion of Austenitic Stainless Steels. J. J. HEGER AND J. L. HAMILTON. *Corrosion*, **11**, No. 1, 22-26 (1955) January.

Results of standard laboratory tests of the corrosion resistance of 18-8 stainless steel indicate the precipitation of minor constituents other than chromium carbide may be significant. Results achieved appear to disagree with those of Bain, Rutherford and Aborn and indicate freedom from intergranular corrosion may be expected only if carbon content is below 0.009 percent, instead of the 0.02 percent they predicted.

Tests showed sensitized 18-8 Mo steel containing 0.03 percent maximum carbon content to be corroded in nitric acid at about the same rates as higher carbon 18-8 Mo steels. Metallographic studies using the corroding solution as an etchant indicated that the delta ferrite-austenite grain boundaries were severely attacked with complete loss of some delta ferrite grains. It is postulated that during sensitization some minor constituent forms at grain boundaries of low carbon

18-8 Mo steels and apparently greater at the boundaries separating the delta ferrite from the austenite.

The need for an instrument capable of making microchemical analyses is mentioned.   8433

6.2.5, 3.8.3, 2.3.9

Oxide Film Composition Studies. T. N. RHODIN, JR. *Annals of New York Academy of Sciences* (Symp. on Properties of Surfaces) **58**, No. 6, 855-872 (1954) September 15.

Data on passive films formed on various typical stainless alloys. Description of film stripping procedures and microanalysis of films was given. Results included discussions of compositional and structural characteristics of surface films, effect of surface treatment on surface composition and surface enrichment of silicon. Tables, graphs, 42 references.—INCO.   8714

6.2.5, 4.6.7, 3.5.9, 3.5.7
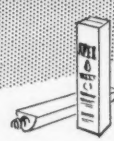
Corrosion of Stainless Steels in Supercritical Water. H. A. PRAY AND W. K. BOYD. Battelle Memorial Inst., Contract W-7405-eng-92 (BMI-901), 20 pp., Feb. 4, 1954.

The corrosion behavior of 10 stainless steels (representing hardenable and nonhardenable grades) has been determined by static tests in degassed supercritical water at 800, 1000 and 1350 F at a pressure of 5000 psi. The materials were evaluated on the basis of weight gain and metallographic examination of sample after exposure to the selected test conditions. The Armco 17-4PH, Armco 17-7PH, and Hastelloy F alloys were the most resistant materials at both 1350 and 1000 F. Inconel X, Type 302 stainless and Allegheny A-286 were severely attacked at both 1350 and 1000 F, whereas the Hastelloy X and Type 410 stainless show heavy attack at 1350 F only. The Type 347 stainless steel, although exhibiting only moderate weight gains, was severely pitted after exposure at 1350 F. Some pitting was also observed on the sample of Type 309 stainless. In supercritical water + hydrogen at 1000 F, the Allegheny A-286 alloy was the only material showing a significant reduction in corrosion resulting from the presence of hydrogen. All the alloys tested had excellent resist-

ance to 800 F degassed supercritical
water after an 84-day exposure. In gen-
eral, the corrosion in degassed super-
critical water at 1350 F was intergranu-
lar in nature, whereas at 1000 F only the
Inconel X material was selectively pene-
trated along grain boundaries. All alloys
suffered some decarburization and carbide
precipitation after exposure at 1350 F.
No decarburization or significant phase
changes were observed for samples ex-
posed at 1000 F. (auth)—NSA.   8442

63 Non-Ferrous Metals and Alloys—Heavy

6.3.6, 4.3.2
**Corrosion Resistant Aluminum
Bronze.** R. J. T. CANEY. Paper before
Australian Inst. Metals, Melbourne
Branch, Sept. 3, 1953. *Australasian Engr.*,
1954, 54-69, June 7.

Experimental work on aluminum
bronze revealed 2 promising alloys con-
taining 90 percent copper and 10 percent
aluminum. One is superior to lead in re-
sisting corrosion by boiling 2½ percent
hydrochloric acid and has mechanical
properties similar to those of mild steel.
A similar alloy is second only to lead in
resisting corrosion by boiling dilute sul-
furic acid. Both alloys can be forged,
hot rolled and extruded. Heat treatment
is necessary to develop full corrosion re-
sistance in boiling 2½ percent hydro-
chloric acid. Neither alloy is suitable
for use at high velocities (40 feet per
second). Extensive tables and graphs
shows results of corrosion tests. Many
of the alloys contain nickel.—INCO. 8072

6.3.6, 6.2.1, 6.3.10, 6.4.1
Magnetic Permeability of So-Called

"Non-Magnetic" Metallic Materials. M.
R. GROSS. *J. Am. Soc. Naval Engrs.*, 66,
No. 1, 215-245 (1954) February.

Presents the results and conclusions
obtained from a large number of perme-
ability tests and discusses the behavior
of various classes of materials. Materials
tested were brasses, bronzes, copper-
nickel alloys, copper, nickel, aluminum
and magnesium base alloys, and stain-
less and manganese steels. Illustrations
and references.—INCO.   8206

6.3.8, 5.3.4
**Plating on Lead Alloys, Pewter and
Britannia.** J. HAAS. *Metal Fin.*, 52, No. 4,
56-61, (1954) April.

Buffing, cleaning, acid dipping, elec-
trodepositing silver and chromium by
various methods, general practice for
holloware, avoiding blistering.—BNF.
8088

6.3.15, 3.4.6, 3.5.9, 3.2.3
**Behaviour of Titanium in Gases at
High Temperatures.** (In Italian). P. SPI-
NEDI. *Alluminio*, 23, No. 1, 35-39 (1954).

Oxidation of titanium in oxygen, car-
bon dioxide and nitrogen atmospheres
studied by measuring weight increase on
heating at 600-930 C. 11 ref.—BNF. 8744

6.3.15, 3.5.9, 3.7.2, 3.7.3
Titanium-Silicon Alloys. D. A. SUT-
CLIFFE. *Rev. Met.*, 51, No. 8, 524-536
(1954).

As part of an investigation on the effect
of certain impurities on the properties of
titanium, a study of the binary alloys of
titanium and silicon was undertaken to
determine i) the maximum quantity of
silicon that will not seriously impair the
working properties of titanium, and ii)
the properties at elevated temperatures.
Alloys containing >2% silicon were pre-

pared fro
taining up
iodide tita
form of
ment. A
previously
taur, Corr
used for
to 875 C.
SiO_3 amp
were dro
For temp
specimen
ceptacles
librium
measuremen
sen's [*Tr*
(1952)],
perature
β-titanium
C. The in
the alloys
to hot f
5.5% silic
draw, and
5.5% silic
silicon i
elevated
temperat
tures UT
to a max
silicon. 5
a rapid f
a linear
hardness
peratures
applies o
silicon. 7
of silicon
the β ph
of 1320 ±
temp, be
solubility
at the c
titanium-
gram is
0.92% si
quenchin
creases
tion at 8
be tolera
1.5%; bu
worked,
sible as
Addition
best all
MA.

6.3.15, 3.
Weldn
nese She
Welding
(1954) A
Influer
coming
commerci
taining
surface

6.3.15, 5.
How t
KIN. *Me*
A stud
oxides f
forging
uation
reported

6.3.15, 7.
Titani
BERG. Pa
Titanium
1954. *M*
46, 48, 5
Super
air corro
nium h

pared from Kroll titanium; those containing up to 2% silicon from remelted iodide titanium. The silicon was in the form of powder purified by acid-treatment. A modification of the arc furnace previously described [Bickerdike, *Metaux, Corrosion-Ind.*, **26**, 314 (1951)] was used for melting. For heat-treatment up to 875 C, the specimens were sealed in SiO_3 ampoules, which, for quenching, were dropped into water and broken. For temperatures above 1000 C, the specimens were placed in titanium receptacles in a vacuum furnace. The equilibrium diagram derived from these measurements agrees well with Hansen's [*Trans. Am. Soc. Metals*, **44**, 518 (1952)], except as to the eutectoid temperature and the solubility of silicon in β-titanium at temperatures up to 1100 C. The investigation of the properties of the alloys showed that: 1) It is possible to hot forge alloys containing up to 5.5% silicon. 2) It is possible to work, draw, and shear alloys containing up to 5.5% silicon. 3) The hardening effect of silicon is proportionately greater at elevated temperatures than at ordinary temperatures. 4) At ordinary temperatures UTS of titanium increases from 25 to a maximum of 52 tone/in. at~3.8% silicon. 5) The addition of silicon causes a rapid fall in the resilience. 6) There is a linear relation between the Vickers hardness and the UTS at ordinary temperatures; at elevated temperatures this applies only to alloys containing $\geqslant 0.5\%$ silicon. 7) The limit of solid solubility of silicon in titanium falls from ~3% in the β phase at the eutectic temperature of 1320 ± 6 C. to 0.65% at the eutectoid temp. between 862 and 848 C; the max. solubility of silicon in $\propto$-Ti is 0.45% at the eutectoid temperature. 8) The titanium-rich side of the equilibrium diagram is of the eutectoid type. 9) The 0.92% silicon alloy was hardened by quenching. 10) The addn. of silicon increases resistance of titanium to oxidation at 800 and 1000 C. 11) Silicon can be tolerated as a simple impurity up to 1.5%; but if the metal is to be cold-worked, the maximum silicon permissible as the sole impurity is 0.25%. 12) Addition of 1.75% appears to give the best all around results. 10 references.— MA.   8704

6.3.15, 3.7.3
Weldments in the Titanium-Manganese Sheet Alloy RC-130A. H. M. MEYER. *Welding J.* (N. Y.), **33**, No. 8, 417s-421s (1954) August.

Influence of heat-treatment in overcoming embrittlement in weldments in commercial titanium alloy sheet (containing 6.5-8% manganese); effect of surface contamination.—BNF.   8624

6.3.15, 5.9.2
How to Descale Titanium. A. E. DURKIN. *Metallurgia*, **49**, 256 (1954) May.

A study was made of the removal of oxides formed by heat treatment and forging operations on titanium. An evaluation of several descaling baths was reported.—NSA.   8410

6.3.15, 7.1, 7.3
Titanium in Jet Engines. D. C. GOLDBERG. Paper before Am. Ordnance Assoc., Titanium Seminar, Fort Worth, May, 1954. *Modern Metals;* **10**, Nos. 10 & 11; 46, 48, 50, 52; 42-43 (1954) Nov., Dec.

Superior resistance to salt water and air corrosion and light weight of titanium have led to its use by engine

manufacturers for compressor discs, compressor blades and vanes, turbine housings, fire shields and other parts. Favorable results of tests made on compressor disk forgings by du Pont and Westinghouse in 1949 indicated that if fabricating problems could be solved economically, titanium would be valuable in engine design. Continued study of the three main alloy systems, alpha, beta and alpha-beta is being made. Limited experimental and production data indicates that titanium in the annealed, unalloyed form behaves like ¼-hard stainless steel, while the alloy grades are similar to the ½-hard grade. Problems encountered in forming, drawing and welding operations are described and forging techniques and machining factors are discussed. Additional research on interstitial elements (oxygen, nitrogen, carbon, hydrogen) must be successfully completed to make titanium more useful to designers. Illustrations, tables.—INCO.   8505

6.4 Non-Ferrous Metals and Alloys—Light

6.4.2, 3.7.3, 2.2.2

Corrosion Tests on Aluminium Alloys. E. M. MULDERS, W. G. R. DE JAGER, AND J. W. BOON. Rept. Metal en Corrosie Inst. T.N.O. (France), 36 pp., 1954.

Pure aluminum and eight different aluminum alloys treated in various ways (welded, soldered, anodized, Alclad) are exposed to outdoor and accelerated laboratory corrosion and the weight variations determined. The method of welding (argon arc, autogenous, spot, etc.) does not affect the corrosion resistance. Best resistance is shown by an Alclad aluminum-zinc-magnesium-copper alloy, provided that aluminum alloy and not coated steel rivets are used for bonding it.—ALL.   8584

6.4.2, 3.7.3, 3.4.8

Sub-Grain Boundary Corrosion in High-Purity Aluminium. M. METZGER AND J. INTRATER. *Nature*, 174, No. 4429, 547-549 (1954) September 18.

Sub-grain boundaries of properly heat-treated specimens of high-purity aluminum are particularly susceptible to corrosion by 7% hydrochloric acid containing about 0.5 ppm. of copper added as cupric chloride. The attack is deep and selective. The sub-grain boundary corrosion is dependent on heat treatment; it is minimized by a rapid quench and increased by an insufficient quench from annealing temperatures. The dependence on heat treatment is presumed to involve the tendency of impurity atoms to concentrate near these boundaries.—NSA.   8632

6.4.2, 3.8.3, 5.9.4

Contributions to the Action of Alkaline Solutions on Aluminium and Aluminium-Alloys. (In German). WILLI MACHU AND M. KAMAL HUSSEIN. *Werkstoffe u. Korrosion*, 5, No. 8/9, 295-301 (1954) August/September.

High purity aluminum cannot be passivated in 1.16 N sodium hydroxide solutions at 90 C even when high current densities of several amp./sq. cm. are used. At smaller sodium hydroxide concentrations a protective layer is produced which is indicated by a rapid decrease in current caused by passivation. The covering layer is quickly destroyed by addition of chlorine ions. For aluminum-magnesium alloys a passivation is possible with 1.16 N sodium hydroxide. Passivity is favored by decreasing sodium hydroxide-concentrations. A covering layer is already formed on aluminum-magnesium alloys by chemical reaction of the sodium hydroxide and is only increased by anodic treatment. The difference in the behavior of aluminum-magnesium alloys is due to formation on the metal surface of alkali-soluble aluminum hydroxide as well as magnesium oxide and magnesium hydroxide, both insoluble in alkali. The higher porosity of the passivating covering layer on the magnesium-aluminum alloy at sodium hydroxide concentrations higher than 0.01 N is based on the fact that aluminum hydroxide and aluminum oxide are not fully protected by magnesium oxide and magnesium hydroxide from being dissolved. The activating effect of chlorine-ions on high-purity aluminum is much stronger than on aluminum-magnesium alloys where the passivating effect of sodium hydroxide on aluminum-magnesium alloys outweighs the activating effect of chlorine-ion. The passivity caused by magnesium oxide and magnesium hydroxide is strong enough not to be destroyed by higher chlorine ion concentrations. As in the case of sodium carbonate, the chemical dissolution power on aluminum is so small that the oxide layers are not as easily destroyed as with sodium hydroxide solutions. Therefore, passivity is easily obtained. It is concluded that it is not possible to reduce by anodic treatment or formation of protective layers the amount of metal removed by alkaline treatment, since passivation is not possible at concentrations used in the alkaline treatment.—ALL.   8708

6.4.3

Preparation, Properties and Uses of Beryllium. E. J. BOYLE AND J. L. GREGG. Oak Ridge National Lab., *Chem. Eng. Progr.* Symposium Ser. No. 11, Part I, Nuclear Engineering, 53-6 (1954).

The properties and preparation of beryllium are discussed, including corrosion resistance to atmosphere and water, solubility in hydrochloric, sulfuric and nitric acids, mineral beryl ($Be_3Al_2Si_6O_8$) sources

preparation by reduction of a molten mixture of sodium chloride and BCl_3 and magnesium reduction of BF_3, vacuum melting, crushing, powder compacting by vacuum hot pressing, mechanical properties of vacuum-hot pressed beryllium before and after warm and hot extrusion and its uses as a moderator in reactors.—NSA.   8501

6.4.4, 8.9.2

Magnesium Die Castings Enter the Automotive Field. E. L. SCHAPER. *Precision Metal Molding,* **12,** No. 9, 58-59, 114-115 (1954) Sept.

The use of magnesium die castings has increased over the past five years, with the greatest gain being in the automotive field. A part of this activity is attributed to periodic shortages of zinc and aluminum, although the change was made to magnesium without a change of dies and some cases have shown a cost saving over the other metals. Performance of a large number of parts has indicated qualities of excellent corrosion resistance; conditions of service included three years under all conditions, including salt road splash. The most commonly used magnesium die casting alloy is Dowmetal RC or ASTM AZ91A. The presence of 0.0003-0.001% beryllium in magnesium die castings has been found to reduce oxidation when the metal is in the molten state and to reduce the normal melting loss by as much as 30%. Magnesium can be used on any piece of machinery having reciprocating parts to reduce inertia and lower power costs.—ALL.   8679

6.4.2, 3.3.4

Preliminary Research on the Possible Influence of Bacterial Metabolism on the Corrosion of Aluminium by Stagnating Water. (In Italian). L. RANUCCI-GATTO. *Alluminio,* **23,** No. 4, 399-411 (1954) July.

Corrosion phenomena on aluminum containers filled with stagnant water, which were not explainable as caused by the water itself, were studied in the light of bacterial influence. In the present article preliminary results of the research work are presented. Different forms of corrosion attack are illustrated and a general theory is outlined on bacterial corrosion. The action of the microorganisms on metals is explained as due to the influence of bacterial metabolism. Reaction mechanisms for different types of bacteria are described. After examining the corrosive action of normal and sterile drinking water and the behavior of the most common bacteria in contact with metals, the effect of sulfur reducing bacteria on aluminum has been studied. The results did not show any significant influence of the common types of bacteria on the corrosion of aluminum. However, from the actual state of the investigation it is not possible to deduct final conclusions.—ALL.   8745

6.4.2, 3.5.8, 5.11

How to Prevent Stress - Corrosion - Cracking in Aluminum Parts. R. N. HOOKER AND J. L. WAISMAN. *Iron Age,* **174,** Nos. 11 & 12, 123-125-165-167 (1954) Sept. 9, Sept. 16.

Redesign to prevent stress build-up after assembly, use of properly fitted components in assembly, and protective coatings to prevent air metal contact. Types of aluminum alloy protective coatings tested: 1) covers metal completely to keep corrosives from contacting base metal, 2) acts anodically to pre-

vent electrolytic corrosion. Photographs, micrographs, charts.   8479

6.4.2, 3.2.3
The Oxidation of Aluminium-Magnesium Alloys by Steam: A Contribution to Research on Mould Reaction. MARJORIE WHITAKER. Appendix: The Constitution of Oxide Films Formed at High Temperature on Aluminium-Magnesium-Beryllium Alloys. A. R. HEATH. *J. Inst. Metals,* **82,** Pt. 3, 107-114, appendix: 114-116 (1953) Nov.

The work described formed part of a research on methods of preventing the reaction between aluminum-10% magnesium alloy and the steam atmosphere generated in a sand mould, a reaction causing surface oxidation and gas porosity in the casting. To reproduce conditions giving rise to this reaction, small cylinders of alloys were heated in steam in a laboratory apparatus and the amount of reaction was assessed by the change in weight. Tests on alloys containing 0.0001-0.15% beryllium, the element usually added to inhibit mould reaction, disclosed minimum reactivity at 0.004% beryllium, suggesting that this is the optimum addition. The rate of oxidation in the laboratory test obeyed a log law. Reducing the moisture content of the atmosphere in the apparatus by dilution with argon decreased the reaction. Investigation of the effect of impurities on the inhibiting action of beryllium showed sodium to be the only harmful one, iron, silicon, copper, calcium, potassium and carbon being innocuous. Prior degassing of the metal with nitrogen, chlorine and hexachlorethane, the use of melting fluxes based on chlorides of potassium and magnesium and grain-refining additions of titanium and boron were also harmless. Small additions of cerium, niobium, tantalum, thorium, vanadium and zirconium, selected on account of the properties of their oxides, had some inhibiting effect on the reaction, both in the presence and absence of beryllium, but it was too small to have any practical application in the foundry. From the results of electron-diffraction and electron-microscope examinations of oxide films it appeared unlikely that the protective action of beryllium could be attributed to a single-phase layer of beryllia in the film. (auth).—MA.   8016

7. EQUIPMENT

7.1 Engines, Bearings and Turbines

7.1, 4.4.7
Designing Performance Into Motor Oil. L. RAYMOND AND J. F. SOCOLOFSKY. Paper before Nat. Petrol. Assoc., Ann. Mtg., Atlantic City, September 16, 1954. *Petroleum Refiner,* **33,** No. 10, 110-115 (1954) October.

One objective of the new motor-oil development by the Socony-Vacuum Oil Co. was the reduction of corrosive wear. Greater use of cars for short trips has increased conditions favorable to corrosive attack, as short trips do not permit reaching high enough jacket temperatures to prevent condensation of corrosive combustion products on the ring and cylinder surfaces. New oils, differing in viscosity characteristics and additive level have been developed in an attempt to decrease wear. Graphs point out effects of motor oils and yearly car mileage on engine wear.—INCO.   8727

CORBAN

Polar-type DOWELL inhibitor checks expensive well corrosion with a protective molecular film

In oil, gas or gas condensate wells, a program of Corban® treatments can prevent literally thousands of dollars of needless equipment replacement. Dowell's modern, polar-type inhibitor, can virtually end costly corrosion damage . . . thanks to a protective molecular film.

Available in both liquid and stick forms, inexpensive, easy-to-use Corban mixes readily with well oil or brine. Passing freely through well tubing and valves, it places a tough, invisible shield of molecules on every metal surface it touches . . . and, as long as treatment continues, Corban sustains this protective film. In addition, Corban entirely avoids the emulsion difficulties associated with some anti-corrosion treatments.

To buy Corban, or for treatment recommendation or more information, call any of the 165 Dowell offices in the United States and Canada; in Venezuela, contact United Oilwell Service. Or write Dowell Incorporated, Tulsa 1, Oklahoma, Department I-77.

services for the oil industry ◆ **DOWELL** ◆

A SERVICE SUBSIDIARY OF THE DOW CHEMICAL COMPANY

• PIG IRO